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Joule Thomson effects for a hydrogen-methane mixture

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A Thesis

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This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

July 1, 1983
Date

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This work is dedicated to my family. Through all the trials and tribulations, they always remained in my corner.

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1. ABSTRACT

A specially designed throttling valve was employed in a closed recirculating system so as to measure the Joule-Thomson coefficient of pure nitrogen and two mixtures of hydrogen and methane. The mixtures had the composition of .127/.873 mole fraction and .5657/.4343 mole fraction of hydrogen/methane. The valve was designed to minimize kinetic and anisenthalpic effects. Nitrogen was used to check the reproducibility of the data obtained by correlating previous results to present work over the pressure range 135.83atm to 21.39atm and a temperature range of 294.87K to 274.38K

Four experimental isenthalps of each mixture were obtained over the ranges of 74.83atm to 5.109atm and 245.60K to 133.57K. The isenthalps were fitted to a third order polynominal and then this polynominal differentiated to obtain the experimental coefficients. The experimental coefficients were compared to the Redlich Kwong equation of state as originally proposed, with the Prausnitz modification and with the Soave modification, and to the Peng-Robinson equation of state. The theoretical coefficients were obtained by using the data points in the appropriate equation of state with mixing rule or modification indicated . The data of Benham and Katz gave boundries for the two phase region.[2] The experimental coefficients were compared to those obtained by Eakin, et. al.[6].

For the rich hydrogen mixture, the Peng-Robinson equation of state gives excellent results when the Prausnitz correction for critical properties is employed. For the methane rich mixture, no equation of state predicted the entire range adequately, and no recomendation for one nor the other can be made. It is apparent however, that the original Redlich-Kwong equation does correlate well when the mixture is not on the verge of entering the two phase region. For all data, the Peng-Robinson equation showed the lowest deviation at 3.36%. The Redlich-Kwong equation with the Prausnitz modification was next with 4.28%, then the Soave modification with 4.86% and finally the original Redlich-Kwong equation with 6.51%

2. INTRODUCTION

Joule Thomson coefficients are quite useful as a measure of the applicability of equations of state and correlations to certain systems. The pure components of methane and hydrogen have been studied extensively, however, mixture data for this system is noticably absent from the literature. Hydrogen and methane are comparatively simple molecular gases, but the quantum interaction of the hydrogen in the mixture causes effects that are usually not predicted by most equations of state. The correlation of the Joule Thomson coefficient of the mixtures to the predicted values of an equation of state gives a rough measure of these quantum effects. In addition, better parameters for the state equations could be derived so that other thermodynamic properties could be predicted with greater accuracy.

This investigation produces data from the region close to the saturation curve and strives to correlate the data to the Redlich- Kwong and Peng-Robinson equations of state. A mumber of mixing rules and modifications were used to represent the theoretical treatment. The objective is to find the best equation of state and mixing rule by correlating experimental coefficients to theoretical, so that this equation and mixing rule could be used to predict other thermodynamic functions for these mixtures.

3. HISTORICAL BACKGROUND

Thermodynamic analysis of the effects of throttling recieved widespread attention in the late nineteeth century. Originally, the investigators were interested in the internal energy of gases. Joule carried out an experiment in 1845 with two large copper vessels connected by a short pipe with a stopcock. One vessel was pressurized while the stopcock was closed,the other was evacuated. The system was immersed in a water calorimeter and the stopcock was opened. The two sides equilibrated with the rush of the high pressure gas to the vacuum side, but no change in temperature was recorded for any gas system used. This was of course due to the high heat capacity of the copper. In addition, the gas, as it is flowing, is in such a turbulent condition that there is no uniformity of pressure or temperature.

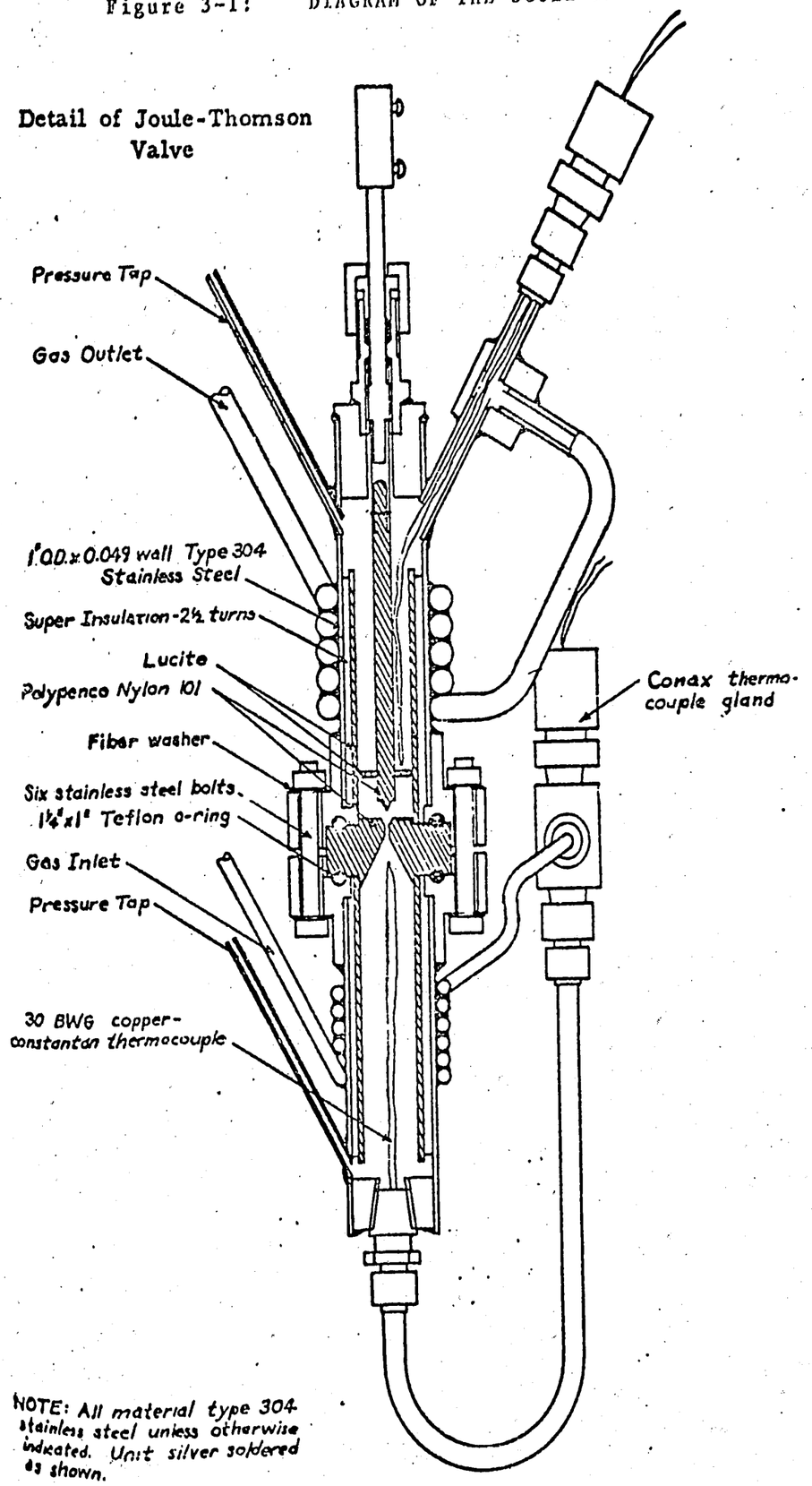
William Thomson, later Lord Kelvin, modified the experiment to avoid these difficulties. He worked with Joule on a series of experiments from 1852 to 1862. Their original experiments were steady flow systems that employed a cotton plug as an obstruction. Heat losses were minimal because they heavily insulated the pipe. They deduced that frictional and kinetic effects were proportional to the square of the flow velocity, and subsequently measured the molal volume, pressue and temperature on both sides of the plug. From this data, they calculated the Joule-Thomson coefficient.[7] It was not for fifty years, however, that reliable data were measured.

Later in the 20th century many investigators modified the original experiment. Hoxton[9] reviews the developments of of this period.

The errors in a radial flow, porous plug apparatus include kinetic effects, and the thermal effects of conduction, convection, and radiation. Roebuck[17] critically analyzed these errors and subsequently produced a set of reliable data for many gases using a porous plug apparatus.

The use of valves, because of their heat capacity, had not been seriously investigated until 1941 when Johnson[10] introduced a major modification of the experiment by using a valve constructed of ebony, wood and monel. It was this valve that Brazinsky[3] used as a model and further refined the design. This valve, however, did not work well for large pressure differences. Stockett[19] improved the valve further, by using heavier gauge thermocouple wires and inserting the wires directly in the gas stream. There still existed a problem of heat conduction through the high and low pressure sides of the valve. Ahlert[1] remedied this problem by using teflon seals between the stages and this last modification proved to be quite successful in experimentation. This was the valve used in this work and is shown as figure 3-1.

Figure 3-1: DIAGRAM OF THE JOULE-THOMSON VALVE



NOTE: All material type 304 stainless steel unless otherwise indicated. Unit silver soldered as shown.

4. EXPERIMENTAL APPARATUS

The initial phases of experimentation consisted of a great deal of system rebuilding. The Heise gauges were checked and recalibrated using the Ruska apparatus and the thermocouples were calibrated with the platinum resistance thermometer for the range of expermentation.

A storage tank of two cubic feet held the experimental mixture. The mixture was mixed from pure components supplied by the Air Products and Chemicals, Inc.. Both components were at 99.97% purity, with the impurity being nitrogen. From the storage tank, the gas was fed to a two stage Corblin oil-driven diaphragm compressor that has a maxium discharge pressure of 3600 PSI. Exiting the compressor,the gas passed through a drier that contained Linde molecular sieve type 3A. No components were absorbed by the drier, however it tended to dampen the pressure oscillations that occurred from the staging of the compressor. After leaving the drier, the gas passed through a countercurrent coil heat exchanger in which the hot high pressure gas was cooled by the low pressure stream exiting from the JT valve. The gas then flows through a constant temperature bath which brought the gas to the desired inlet temperature . The bath consisted of a two gallon dewar in which Freon-11 was used as the fluid. The coolant was liquid nitrogen, used both directly and through a coil immersed in the freon. Heat was supplied by a resistance immersion blade. The temperature control was maintained by a Bayley Precision controller which activated the heater

blade when required. Bath agitation was maintained by a Fisher variable stirrer or by the vaporization of the liquid nitrogen.

After the contant temperature bath, the gas was transferred to the JT valve by a heavily insulated copper tube. The valve was enclosed in a tank packed with copius amounts of a variety of insulative materials. From either side of the valve, there is a pressure tap and a Conax gland for the thermocouples. Exiting the valve, the gas passed through the heat exchanger, regulating valves and flow meter, then finally back to the low pressure inlet of the compressor to repeat the cycle. A flow diagram of the system used is shown in figure 4-1.

FLOW PLAN OF J-T APPARATUS

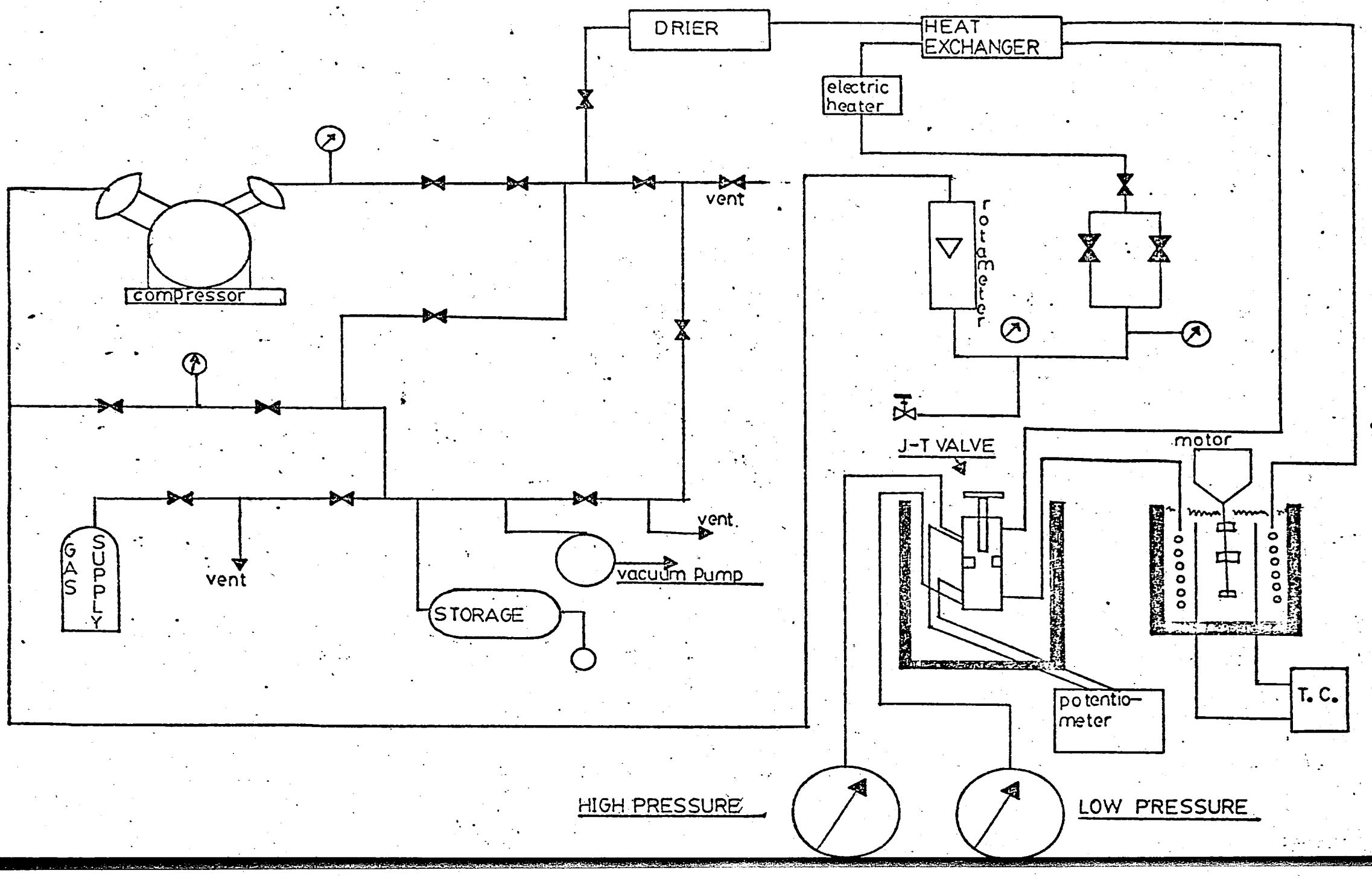


Figure 4-1: FLOW PLAN OF APPARATUS

5. PROCEDURE

The system was charged with the mixture by first evacuating the apparatus to less than two mmHg and then purging with 20 PSI of mixture three times. The storage tank was refilled to 175 PSI after the third purging

Prior to starting the system, the water to the compressor was turned on and the oil level checked. The reference junction for the thermocouples was set up and the temperature controller was turned on to warm up. The constant temperature bath was set up and initially liquid nitrogen was bubbled through so as to get the temperature in the approximate range required.

Compensator pumps and stages to the compressor were primed and the oil level checked. A valve check of the operator board was carried out to be sure the valves were set in the correct positions. The Heise gauges were zeroed and the potentiometer was balanced. The JT valve was opened and the flow regulating valves were closed. The compressor was started and a constant inlet flow was maintained so the interstage pressure did not exceed 11 atmospheres. A pressure greater than this causes undo strain to the thin metal diaphragms. If that pressure is exceeded, the diaphragms could crack or rupture causing oil to enter the system. This occured on the high pressure side once during operation and both high and low pressure diaphragms were replaced.

At start up of the compressor, the drier inlet valve was closed and the circulation loop bypass valve was opened so as to confine the gas to a small region until the compressor warmed up and it was determined that it was not losing prime. There was a one in three chance that prime was lost due to compensator pump valve clogging. After warm up the bypass was shut and the inlet opened. With the regulating valves closed, the pressure increased rapidly. Gas inlet to the compressor was halted momentarily at near 400 PSI so that a sample could be obtained for later analysis.

After the pressure was about 100 PSI greater than desired for the experiment, the flow regulating valves were adjusted so as to get the proper test pressure. The entire system was then allowed to equilibrate and usually did in under three hours. Equilibrium was determined when the pressure did not vary more than 5 PSI and the temperature not more that 2.0K over a period of thirty minutes

At this point the JT valve was partially closed so as to get approximately a 100 PSI kick down in pressure from high to low. After closing, the system was allowed to equilibrate again and usually did in about an hour. During this time the inlet pressure and temperature were held constant, and after equilibrium, the temperature and pressure were recorded. Closing the valve further yielded another data point, and this procedure was repeated five to seven times to generate the isenthalp. Occasionally, the valve could not be closed very far

because the temperature drop was enough to cause a two phase condition. This condition was shown by the oscillation of the pressure while temperature remained nearly constant. When this effect occurred, that data point was not used and other data were taken. Only when there was complete confidence that a truly single vapor phase existed was a data point taken as accurate.

At the end of the experimental session a shut down of the system consisted of opening the JT valve to equalize the pressure. The temperature controller was shut down and a lid was placed over the constant temperature bath. A sample of gas was again withdrawn and the recirculating gas was directed back to the storage tank. Positive pressure was maintained in the system at all times. The compressor was then shut off and the electrical panel shut down. The potentiometer was secured and the batteries disengaged. After the stages to the compressor were cold to the touch the cooling water was shut off. and the system was secured.

Gas analysis was done on a Perkin Elmer 910 Gas Chromatagraph with a 12 foot, 0.25 inch O.D. stainless steel column packed with chromasorb. An Omega strip chart recorder with integrater was used to record output from a thermal conductivity detector. The method of analysis was obtained from a U.S. Bureau of Mines report[11]

6. THEORETICAL BACKGROUND

As with any thermodynamic problem it is best to start the analysis and ultimate solution at the most fundamental point. For this case, that point would be the first law:

$$\Delta H + (\Delta V^2/2g_c) + (g/g_c)\Delta Z = Q - W$$

We adopt as our system the JT valve itself, hence no work is done. We, by design, have minimized the effect of kinetic energy and heat flow. Relative to the valve, the change in potential energy is very small. From this analysis we obtain that the change in enthalpy must be zero. Enthalpy is a state function, and we can write the exact differential thus:

$$H=H(T,P,X)$$

$$dH = (\partial H/\partial T)_p dT + (\partial H/\partial P)_t dP$$

We have neglected the composition differential because there is no change in composition. The first differential is defined as the heat capacity at constant pressure, C_p.

The second differential can be determined using the Maxwell relations as:

$$[\ V-T(\partial V/\partial T)_p]dP$$

hence since dH=0, we arrange the equation and the result:

$$-dT/dP = (1/Cp)*[\ V-T(\partial V/\partial T)_p]$$

This is the definition of the Joule Thomson coefficient (μ) . The equations of state that are applied in this work are the original Redlich-Kwong[15], the Redlich-Kwong with the Soave modification[18], and the Peng-Robinson[13]. The mixing rules applied were the original Redlich-Kwong, and Chueh and Prausnitz[5]. The derivation of the heat capacity equations and the Joule- Thomson expressions for these equations of state can be found in appendix A.

The equations of state are given as:

The Redlich-Kwong equation is given as:

$$P= RT/(\underline{V}-b) - a/(T^{0.5}\underline{V}(\underline{V}+b))$$

They gave the values of the constants, a and b, as:

$$a= 0.42748\ [R^2Tc^{5/2}]/Pc$$

$$b=0.08664\ [RTc/Pc]$$

These were for each pure component. The mixing rules that were employed in the original work:

$$a_m = \sum^{c}_{i=1} \sum^{c}_{j=1} y_i y_j a_{ij}$$

where $a_{ij} = (a_i a_j)^{0.5}$

$$b_m = \sum^{c}_{i=1} y_i b_i$$

The parameter a, as described in the Van der Waals equation of state, is an intermolecular interaction constant. The b parameter is a volume size constant.

Brief and Joffe [4] have shown that the pure components and mixtures of hydrogen and methane follow the Benedict-Webb-Rubin equation of state satisfactory with the constants Brief and Joffe calculated. Redlich, Ackerman, et. al. [14] have calculated constants for the Redlich-Kwong equation of state for methane, and their work has shown excellent agreement.

The original mixing rules were refined by Chueh and Prausnitz [5]. Their work was to derive a better equation for the constants by using an adjustable parameter for the first empirical constants in the original equations for "a" and "b". Gunn [8] and his co-workers proposed a temperature dependence of the critical properties for quantum gases. These dependencies employed a correction utilizing the system temperature and molecular weight of the quantum gas. The corrections were used in the calculations except for the original Redlich- Kwong values.

Chueh and Prausnitz proposed that:

$$a = \Omega_a R^2 Tc^{2.5} / Pc$$

$$b = \Omega_b RTc / Pc$$

$$a_{ij} = (\Omega a_i + \Omega b_j) R^2 Tc_{ij}^{2.5} / (2\, Pc_{ij}$$

$$Pc_{ij} = Zc_{ij}\ R\ Tc_{ij}\ /\ Vc_{ij}$$

$$Vc_{ij}^{1/3} = 0.5(\ Vc_i^{1/3} + Vc_j^{1/3})$$

$$Zc_{ij} = 0.291 - 0.08((\Omega_i + \Omega_j)/2$$

$$Tc_{ij} = (\ Tc_i\ Tc_j)^{0.5}(1-K_{ij})$$

The constant K is a correction factor for the deviation of the geometric mean. The omega parameters are corrections for the correlating constants that Redlich and Kwong originally used. For the present work, the omega parameters were identical to those that Redlich and Kwong used. A list of parameters for methane and hydrogen are supplied in table 8.1.

Giorgio Soave[18] proposed a temperature dependence on the constant a and some changes in the correlating constants.

$$a(T) = a(Tc) * \alpha(T)$$

$$b(T) = b(Tc)$$

$$a(Tc) = 0.42747\ R^2 Tc^2 / Pc$$

$$b(Tc) = 0.08664\ R\ Tc/Pc$$

$$\alpha^{0.5} = 1 + (m(1 - Tr^{0.5}))$$

where m is the slope of the line obtained by plotting:

$\alpha(T)$ vs. $Tr^{0.5}$

The slopes have been correlated as:

$$m = 0.480 + 1.574\omega - 0.176\ \omega^2$$

the cross coefficient is $a_{ij} = (a_i a_j)^{0.5}(1-K_{ij})$

The mixing rules of the original Redlich-Kwong paper are then used.

The temperature dependence of the critical properties of the hydrogen can be expressed as:

$$Tc = Tc^o / [1 + (c1/mT)]$$

$$Pc = Pc^o /[1 + (c2/mT)]$$

c1 and c2 are empirical constants that equal 21.8K and 44.2K respectively.

The equation of state proposed by Peng and Robinson[13] is quite similar to the Redlich Kwong equation.

$$P = (RT/(\underline{V} -b))- [a(T)/\underline{V}(\underline{V}+b) + b(\underline{V} -b)]$$

were $a(T) = a(Tc)*\alpha(T)$

$$a(Tc)=0.45724\ R^2Tc^2/Pc$$

$$\alpha(T)^{0.5} = 1 + k(1-Tr^{0.5})$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

The cross coefficient $a_{ij} = (1-\delta)(a_i a_j)^{0.5}$ the δ must be determined empirically. There exists no reporting of δ for this mixture. It was calculated using P-V-T data that was obtained from Mueller,Leland and Kobayashi[12]

The b parameters were given by Peng and Robinson as:

$$b(T)=b(Tc)= 0.07780\ RTc/Pc$$

The mixing rules are the same as those used in the Redlich-Kwong original paper.

7. RESULTS and DISCUSSION

One can see from the graphs of the isenthalps that the data present smooth curves and the subsequent differentiation to obtain the Joule- Thomson coefficients yields interesting results. With the approximate 50/50 mixture one can see that the Peng-Robinson curves correlate quite closely to the data. The general trend is that as one goes from the original Redlich-Kwong equation to the Prausnitz modification to the Soave modification and finally to the Peng-Robinson equation, the agreement gets better between prediction and data. Interestingly enough for the hydrogen rich mixture, the data fall on both sides of the predicted. None of the equations yields very good correlation in all pressure ranges, however at higher pressures the agreement is better than at low. This leads to the belief that the equations over correct for the quantum interactions at low pressure. The error associated with the hydrogen rich mixtures are: 8.72% for the original Redlich-Kwong equation, with a range of -17.50 to 1.38; 4.21% for the Prausnitz modification, with a range of -9.24 to 9.33; 4.89% for the Soave modification, with a range of -1.86 to 16.25; and the Peng- Robinson equation with 3.21% with a range of -1.18 to 11.38 . The run "3b" is in doubt because of the high error, but is reported.

The methane rich mixture showed, overall, excellent agreement. there is a clear pattern that as one progresses to a later equation or modification, the correlation is improved. The Peng-Robinson equation

does an excellent job of prediction, especially in the higher pressure region. The error associated with this mixture are: 3.89% for Redlich Kwong with a range of -10.00 to 15.00; 3.68% for Prausnitz with a range of -9.43 to 15.68; 3.33% for Soave with a range of -10.43 to 15.74; and 3.11% for Peng Robinson with a range of -11.23 to 13.59.

It is believed that with the methane rich mixture all the equations do a good job of prediction because the quantum interaction is so slight; however, the hydrogen rich mixture causes problems since the equations all under correct at low pressure, then over correct at high pressure. This would seem to be the case, since the quatum effects would be functions of not only temperature, by a kinetic energy approach , but also pressure by a molecular radii concept. The omega parameter takes into account the critical properties in its definition, however, most correlations that use the omega to obtain other parameters are only weak functions of omega. Perhaps better correlations could be obtained if reduced properties were used to formulate the empirical constants.

Agreement to the Eakin data [6] is not found, since they do not report the coefficients, one had to differentiate their data. It was found that for a mixture of 51.048 methane/48.840 hydrogen at an inlet of 1000 psi and -0.50F., the coefficient is .19 k/atm. It is curious that the investigators mention a "lit. value " but do not report the citation. Extrapolation of my data to this range yields a result of

.265 k/atm.

Errors associated with the experimental work are due to inaccuracy in the pressure and temperature readings or calibrations. The Heise gauges, even with a reliable calibration curve, exhibit errors due to hysteresis and readability. These errors are estimated by the recomendation of the manufacturer to be 3 PSI and results in an error in the Joule Thomson coefficients on the order of 0.4%.

The platinum resistance thermometer gave a temperature error in the thermocouples of 0.014K. This error caused an error in the Joule- Thomson coefficient of 0.02%. These temperature and pressure errors are, unfortunately, unavoidable.

Table 7-1: NITROGEN ISENTHALP FOR 294.87K AND 135.83 ATM

Press. ATM	Temperature,K				
	Randelman	Ahlert	Din	Strobridge	Roebuck
135.83	294.88	294.90	298.84	294.99	
107.59	291.21	291.21	291.06	291.54	
82.84	287.21	287.44	287.11	287.93	
73.59	285.93	285.81	285.48	286.43	
62.17	283.37	283.76	283.33	284.45	283.76
44.92	280.03	280.30	279.82	281.18	280.31
31.58	277.09	277.37	276.92	278.43	277.33
21.39	274.93	275.00	274.54	276.48	274.91
0.00	269.55	269.58	269.25	271.04	269.33

Table 7-2: JOULE-THOMSON COEFFICIENTS FOR NITROGEN ISENTHALP

For Isenthalp at 294.78K and 135.83 ATM

Pressure,ATM	Coefficient K/ATM				
	Randelman	Ahlert	Din	Strobridge	Roebuck
135.83	0.110	0.116	0.119	0.110	
107.59	0.143	0.142	0.147	0.134	
82.84	0.172	0.167	0.173	0.158	
73.17	0.183	0.177	0.182	0.167	
62.17	0.196	0.190	0.194	0.180	0.189
44.92	0.216	0.210	0.212	0.199	0.213
31.58	0.231	0.227	0.226	0.215	0.231
21.39	0.243	0.240	0.237	0.227	0.246
0.00	0.271	0.268	0.259	0.254	0.276

Table 7-3: EXPERIMENTAL ISENTHALPS: MIXTURE A

for .127 / .873 mole fraction hydrogen/methane

1A		2A	
Pressure(atm)	Temperature (K)	Press.(atm)	Temp.(K)
66.327	219.44	47.636	198.22
59.199	213.48	41.264	192.64
51.244	208.68	34.769	185.08
47.625	204.03	27.141	178.74
44.230	200.88	20.485	167.72
40.842	197.53	13.764	155.92
34.014	190.31	3.402	133.57
3A		**4A**	
54.429	220.18	71.429	245.60
50.009	216.91	62.934	238.20
44.229	211.72	54.431	235.33
38.791	207.55	42.182	227.38
31.299	200.50	30.967	215.06
25.512	193.31	19.407	203.07
18.636	185.52	5.109	182.98

Table 7-4: EXPERIMENTAL ISENTHALPS: MIXTURE B

for .5657 / .4343 mole fraction hydrogen/methane

1B		2B	
Pressure(atm)	Temperature (K)	Press.(atm)	Temp. (K)
68.027	199.54	71.429	181.63
61.572	198.68	63.272	178.71
57.468	196.09	55.448	176.62
50.148	194.96	47.621	173.86
43.886	192.59	40.148	170.96
38.817	191.21	25.854	164.19
33.002	188.85	13.535	157.87
3B		4B	
74.830	215.25	51.020	204.00
65.660	212.43	43.207	202.00
54.422	210.85	35.378	199.12
44.565	206.97	30.279	197.61
34.017	203.22	24.153	195.72
20.333	198.85	18.369	193.17
5.446	192.58	11.568	190.62

Table 7-5: MIX A JOULE-THOMSON COEFFICIENTS

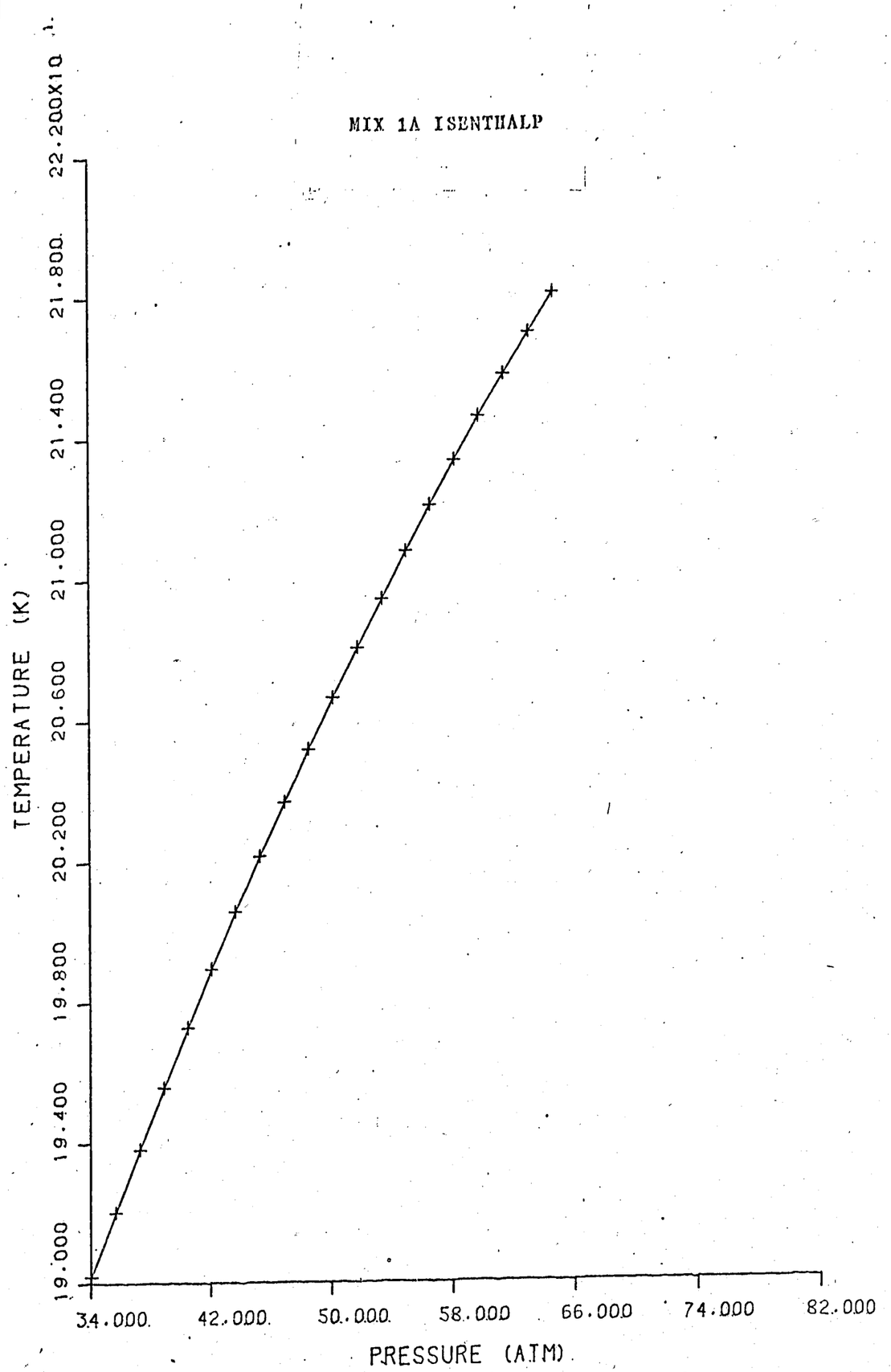
	Joule Thomson Coefficients								
Data	RK	Dev.	RP	Dev.	RS	Dev.	PR	Dev.	
.67566	.66341	1.81	.65697	2.76	.67862	-0.44	.66526	1.54	
.76475	.74010	3.22	.73277	4.18	.75634	1.10	.74265	2.89	
.87535	.82743	5.47	.81905	6.43	.84485	3.48	.83277	4.86	
.92957	.88641	4.64	.87744	5.61	.90501	2.64	.89227	4.01	
.98265	.93756	4.59	.92798	5.56	.95699	2.61	.94469	3.86	Mix 1A
1.03776	.99322	4.29	.98307	5.27	1.01360	2.33	1.0018	3.47	
1.15532	1.12000	3.05	1.10870	4.04	1.14190	1.16	1.1316	2.05	
.92185	.92225	-0.04	.91293	0.97	.94171	- 2.15	.92508	-0.35	
.95425	1.0318	-8.12	1.0212	-7.02	1.0529	-10.34	1.0368	-8.65	
1.0590	1.1710	-10.58	1.1158	-9.43	1.1939	-12.74	1.1780	-11.23	
1.2744	1.3209	-3.64	1.3076	-2.59	1.3422	- 5.40	1.3317	-4.49	Mix 2A
1.5441	1.5516	-0.48	1.5363	0.50	1.5689	- 1.60	1.5572	-0.85	
1.8935	1.8410	-2.77	1.8238	3.68	1.8380	2.93	1.8278	3.47	
2.5841	2.5424	-1.62	2.5211	2.44	2.4081	6.81	2.4054	6.92	
.74761	.73880	1.18	.73132	2.18	.75387	-0.84	.74744	0.02	
.78144	.78494	-0.45	.77701	0.57	.80092	-2.49	.79555	-1.80	
.84045	.85576	-1.82	.84716	-0.80	.87312	-3.89	.86904	-3.40	
.91125	.92195	-1.17	.91280	-0.17	.94036	-3.19	.93866	-3.01	
1.0331	1.0319	0.12	1.0219	1.08	1.0511	-1.74	1.0529	-1.92	Mix 3A
1.1464	1.1439	0.22	1.1331	1.16	1.1624	-1.39	1.1667	-1.77	
1.3029	1.2814	1.65	1.2698	2.54	1.2947	0.63	1.3043	-0.11	
.54671	.54059	1.12	.53507	2.13	.55049	-0.69	.54930	-0.47	
.58381	.60619	-3.83	.60004	-2.78	.61755	-5.78	.61672	-5.64	
.65058	.65753	-1.07	.65096	-0.06	.66981	-2.96	.67265	-3.39	
.79887	.75773	5.15	.75039	6.07	.77221	3.34	.78015	2.34	Mix 4A
.98860	.89951	9.01	.89112	9.86	.91602	7.34	.92819	6.11	
1.2381	1.0646	14.01	1.0553	14.77	1.0787	12.88	1.0990	11.24	
1.6226	1.3791	15.00	1.3681	15.68	1.3672	15.74	1.4020	13.59	

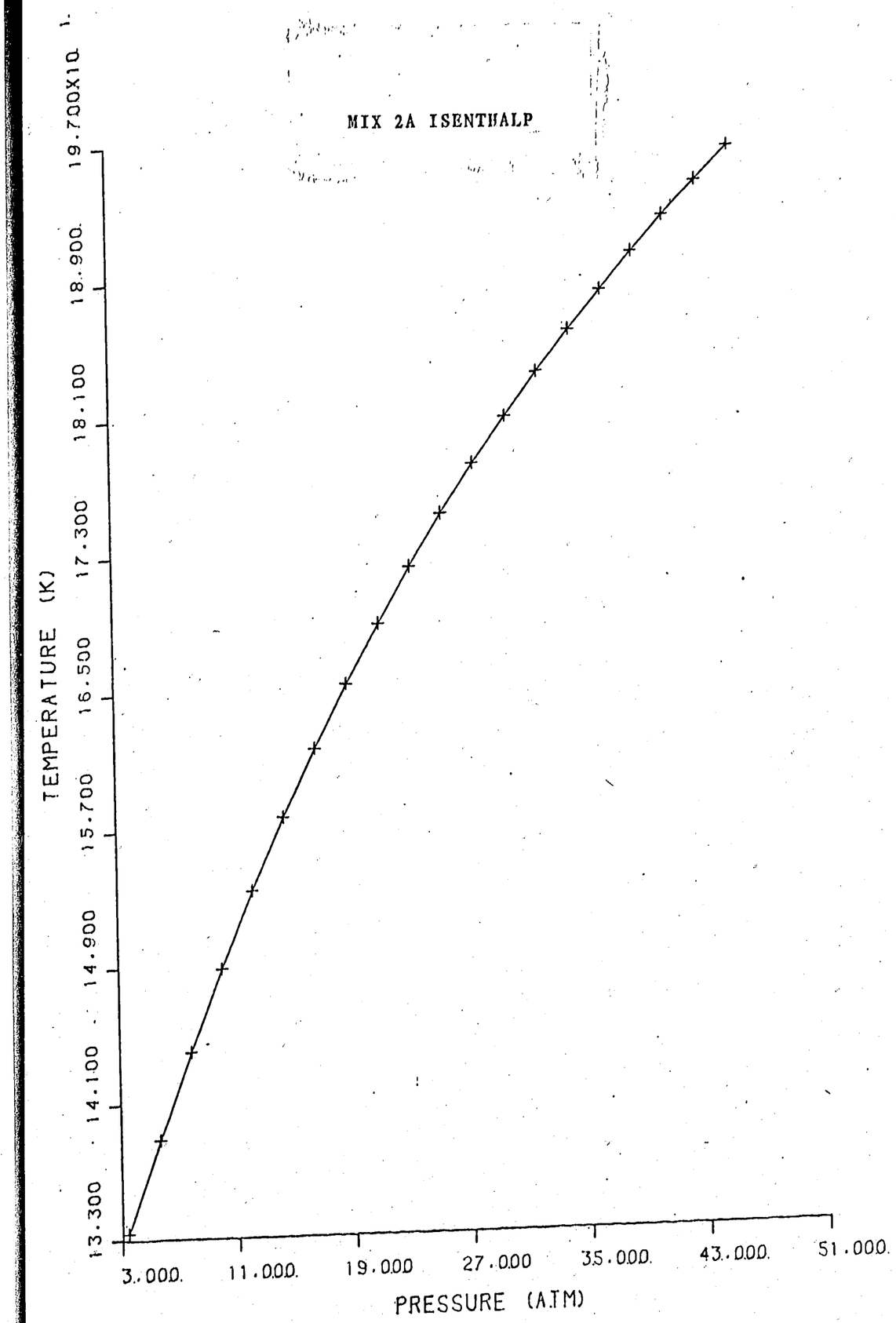
Table 7-6: MIX B JOULE-THOMSON COEFFICIENTS

Joule Thomson Coefficients

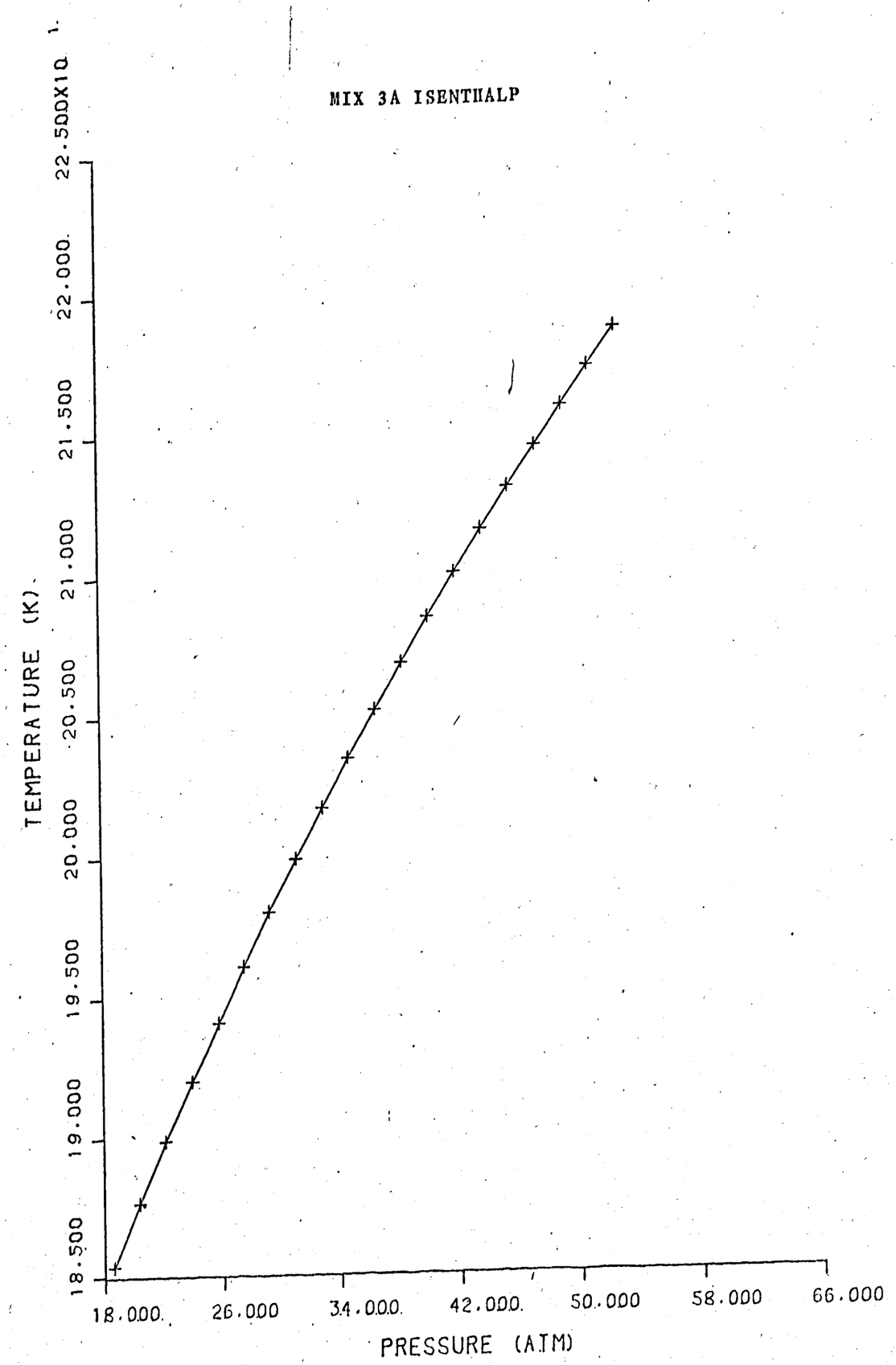
Data	RK	Dev.	RP	Dev.	RS	Dev.	PR	Dev.	
.27354	.30514	-11.55	.28543	-4.35	.26341	3.70	.27424	-.255	
.30008	.32554	- 8.48	.30513	-1.68	.28307	5.66	.29568	1.46	
.32676	.35011	- 7.15	.32886	-0.64	.30697	6.06	.32147	1.62	
.34419	.36543	- 6.17	.34373	0.13	.32213	6.41	.33819	1.74	
.36517	.38471	- 5.35	.36248	0.74	.34141	6.50	.35957	1.53	Mix 4B
.38503	.40695	- 5.69	.38407	0.25	.36363	5.56	.38384	0.31	
.40844	.43215	- 5.80	.40864	-0.05	.38921	4.71	.41233	-0.95	
.20178	.23710	-17.50	.22043	-9.24	.19984	0.96	.20842	-3.29	
.24045	.25752	- 7.10	.23998	0.19	.21874	9.03	.22837	5.02	
.28342	.27929	1.46	.26101	7.91	.23931	15.56	.25116	11.38	
.31712	.30689	3.22	.28754	9.53	.26570	16.21	.27929	11.93	
.34904	.33753	3.30	.31715	9.14	.29559	15.31	.31172	10.69	Mix 3B
.38408	.37859	1.43	.35707	7.03	.33670	12.34	.35736	6.95	
.41402	.43403	- 4.83	.41111	0.70	.39308	5.06	.42002	-1.45	
.28460	.33096	-16.289	.30802	-8.23	.28672	-0.75	.28433	0.09	
.30936	.36227	-17.11	.33768	-9.16	.31511	-1.86	.31303	-1.19	
.33829	.39209	-15.90	.36607	-8.21	.34247	-1.23	.34136	-0.91	
.37232	.42667	-14.60	.39908	-7.19	.37463	-0.62	.37460	-0.61	
.40955	.46331	-13.13	.43416	-6.01	.40912	-0.10	.41046	-0.22	Mix 2B
.49366	.54805	-11.02	.51565	-4.45	.48997	0.75	.49494	-0.26	
.57975	.49494	- 9.46	.59930	-3.37	.57332	1.11	.58351	-0.65	
.26167	.28714	- 9.73	.26746	-2.21	.24606	5.96	.25124	3.98	
.27151	.30191	-11.19	.28165	-3.73	.25975	4.33	.26609	1.99	
.28066	.31796	-13.29	.29692	-5.79	.27469	2.13	.28116	-0.18	
.30229	.33646	-11.30	.31478	-4.13	.29225	3.32	.30039	0.63	Mix 1B
.32640	.35798	- 9.67	.33544	-2.77	.31275	4.18	.32208	1.32	
.34960	.37404	- 6.97	.35089	-0.37	.32832	6.10	.33899	3.05	
.38049	.39639	- 4.18	.37254	2.09	.35002	8.00	.36219	4.81	

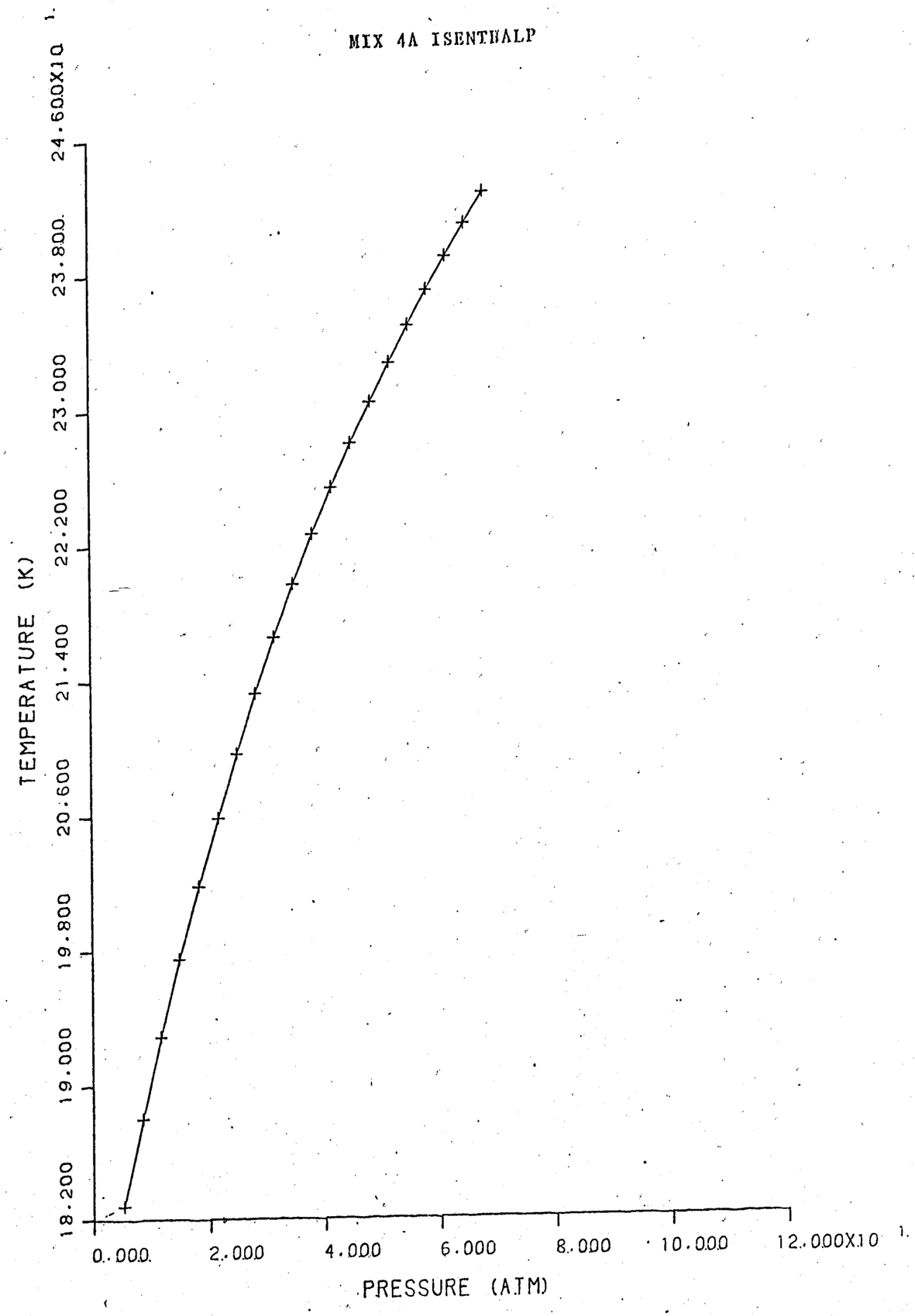
Figure 7-1: EXPERIMENTAL ISENTHALPS


MIX 1A ISENTHALP
TEMPERATURE (K)
22.200X10
21.800
21.400
21.000
20.600
20.200
19.800
19.400
19.000
34.000
42.000
50.000
58.000
66.000
74.000
82.000
PRESSURE (ATM)

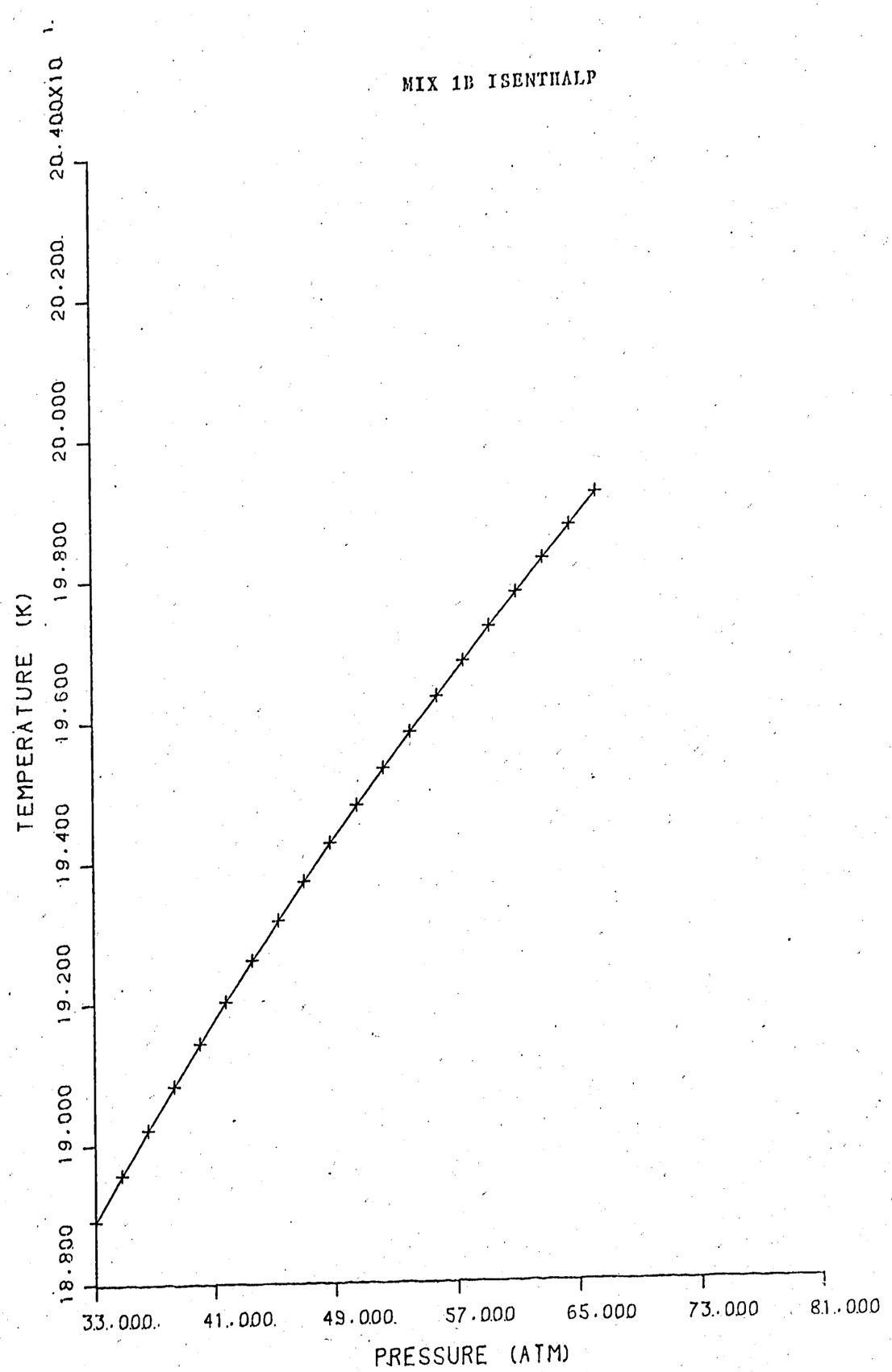

MIX 2A ISENTHALP
19.700X10
18.900
18.100
17.300
16.500
15.700
14.900
14.100
13.300
TEMPERATURE (K)
3.000.
11.000.
19.000
27.000
35.000.
43.000.
51.000.
PRESSURE (ATM)

MIX 3A ISENTHALP

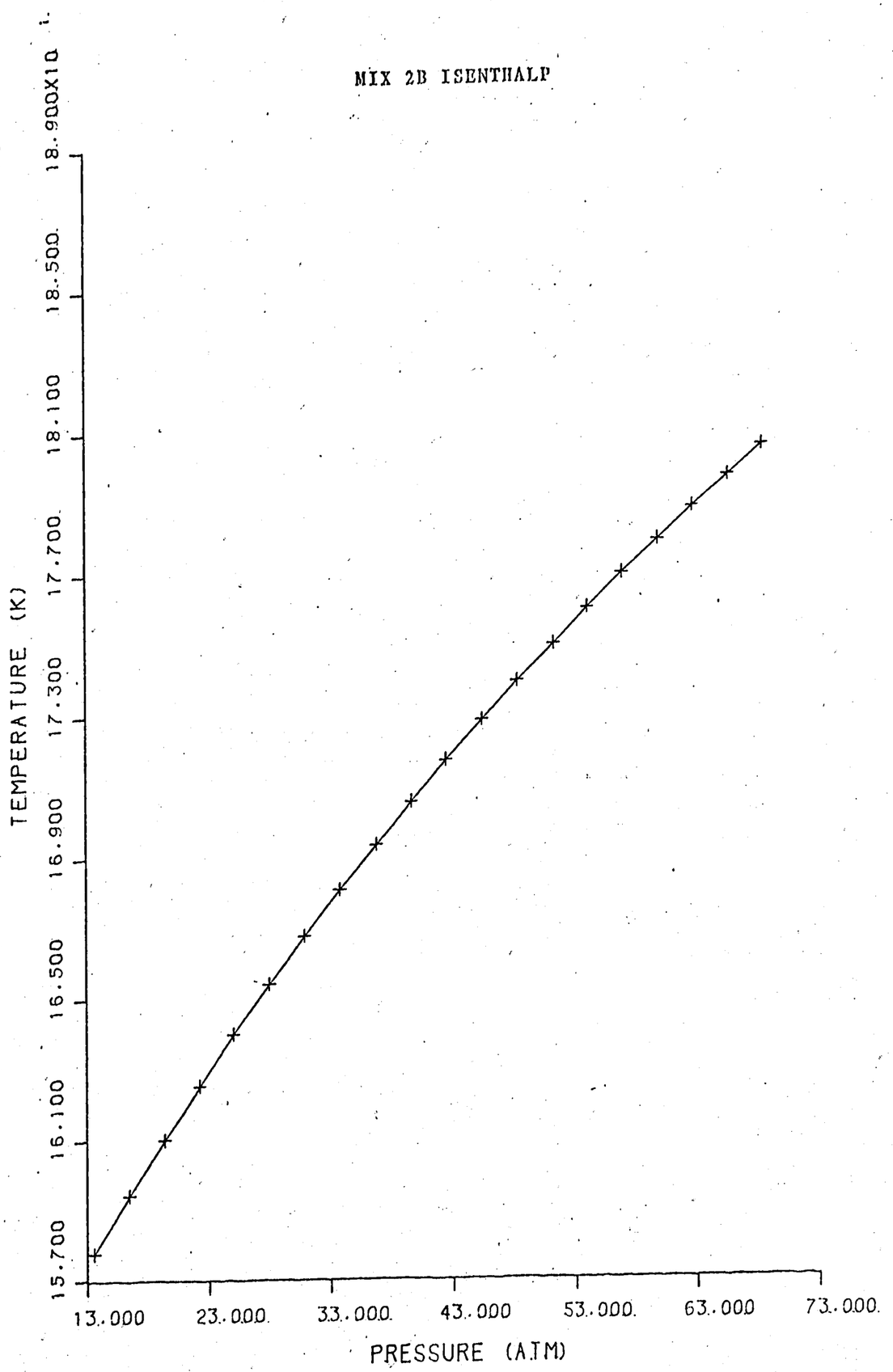


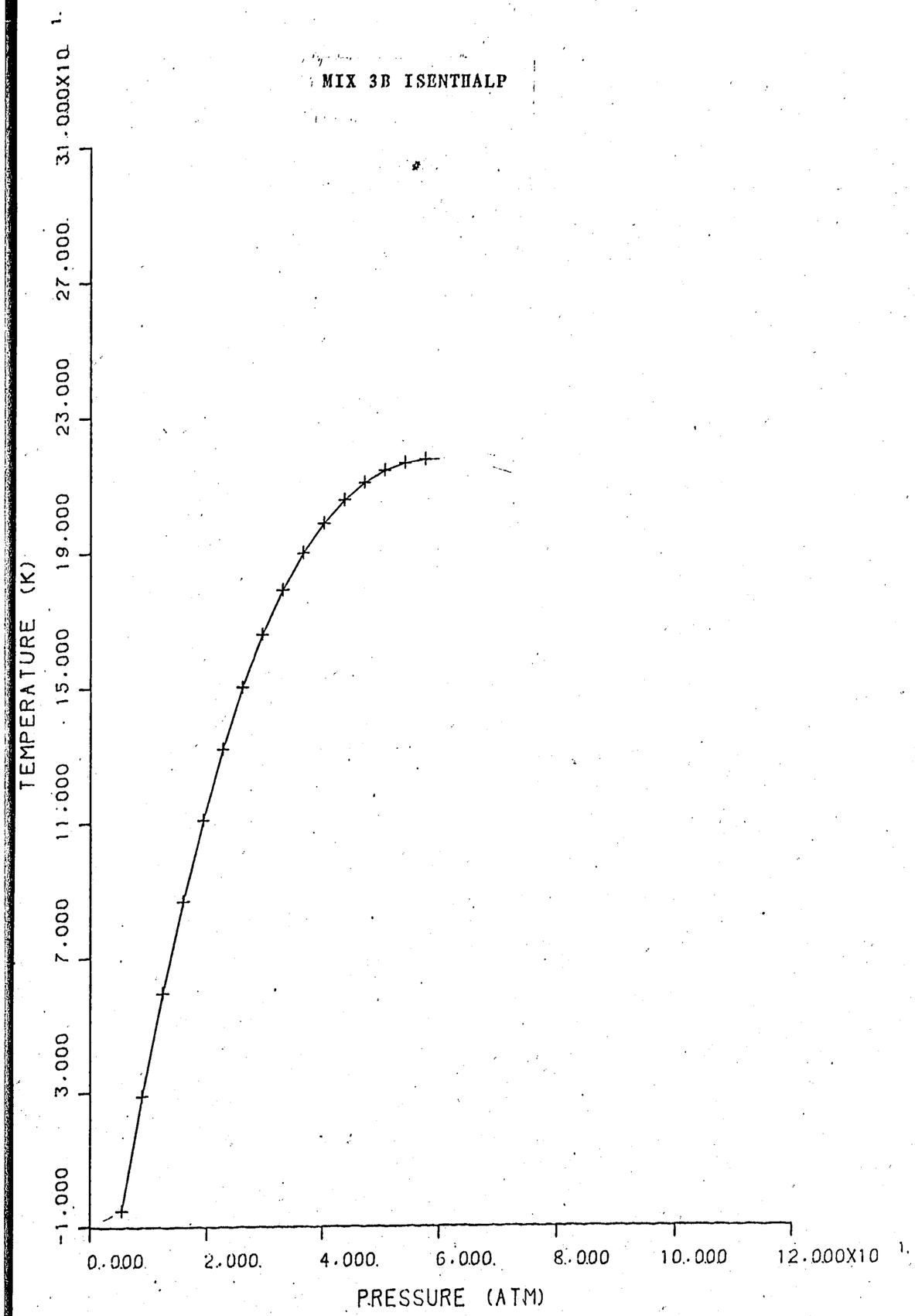

MIX 4A ISENTHALP
TEMPERATURE (K)
18.200
19.000
19.800
20.600
21.400
22.200
23.000
23.800
24.600X10 1.
0.000
2.000
4.000
6.000
8.000
10.000
12.000X10 1.
PRESSURE (ATM)

MIX 1B ISENTHALP



MIX 2B ISENTHALP




MIX 3B ISENTHALP
TEMPERATURE (K)
-1.000
3.000
7.000
11.000
15.000
19.000
23.000
27.000
31.000X10 1.
0..000
2.000.
4.000.
6.000.
8.000
10.000
12.000X10 1.
PRESSURE (ATM)

MIX 4B ISENTHALP

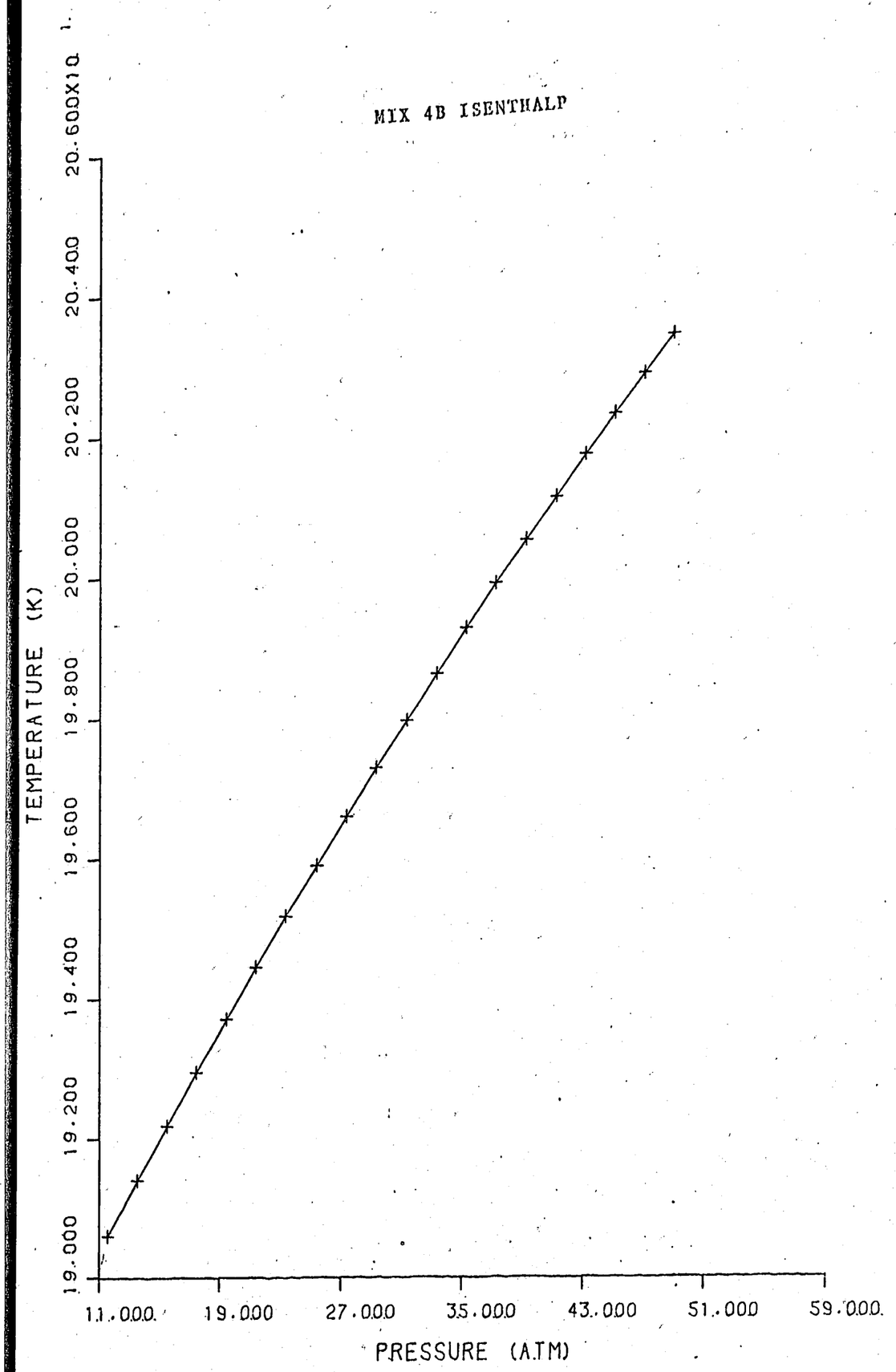
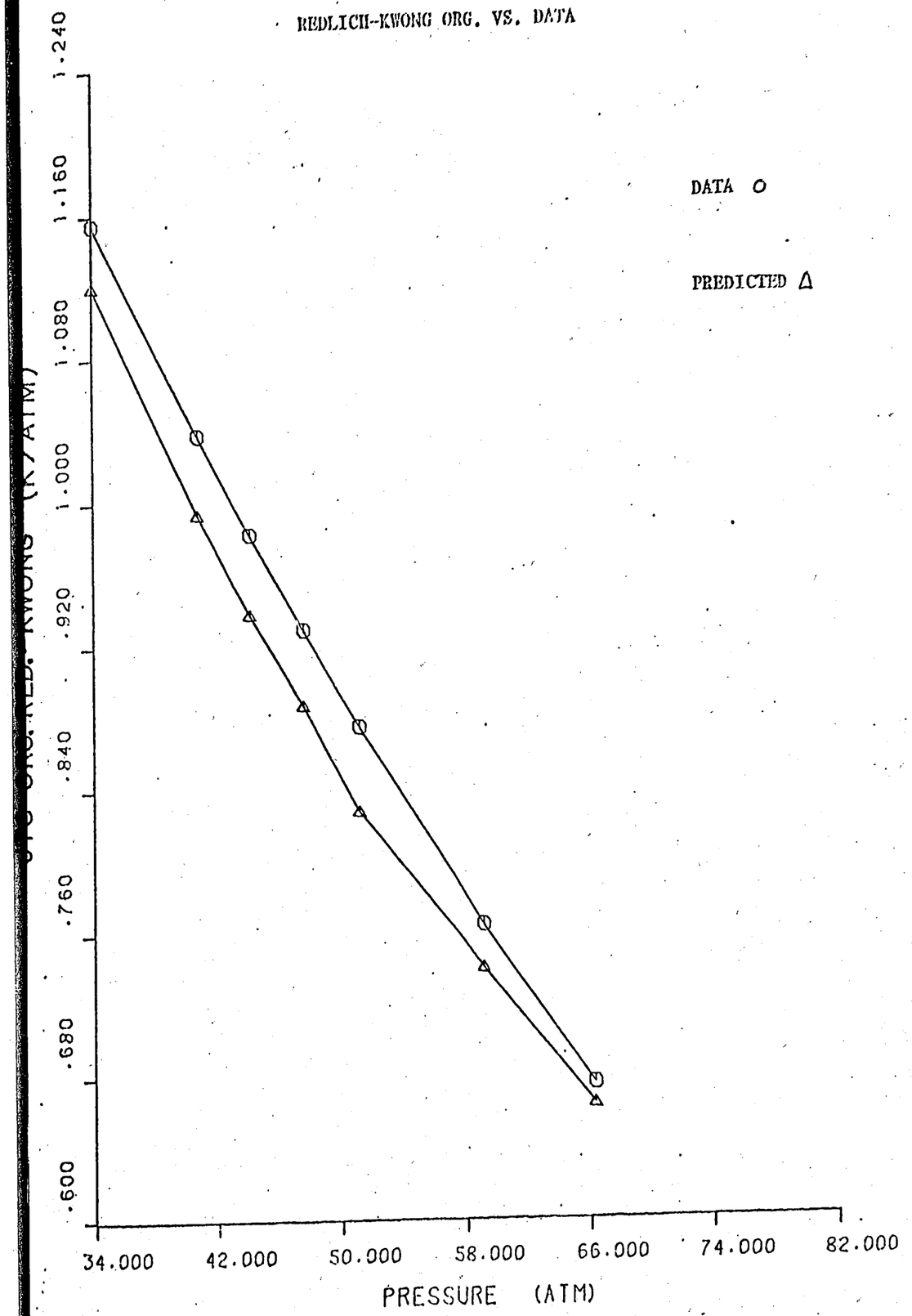


Figure 7-2: MIXTURE A COEFFICIENTS: DATA vs.PREDICTED

JOULE-THOMSON COEFFICIENTS

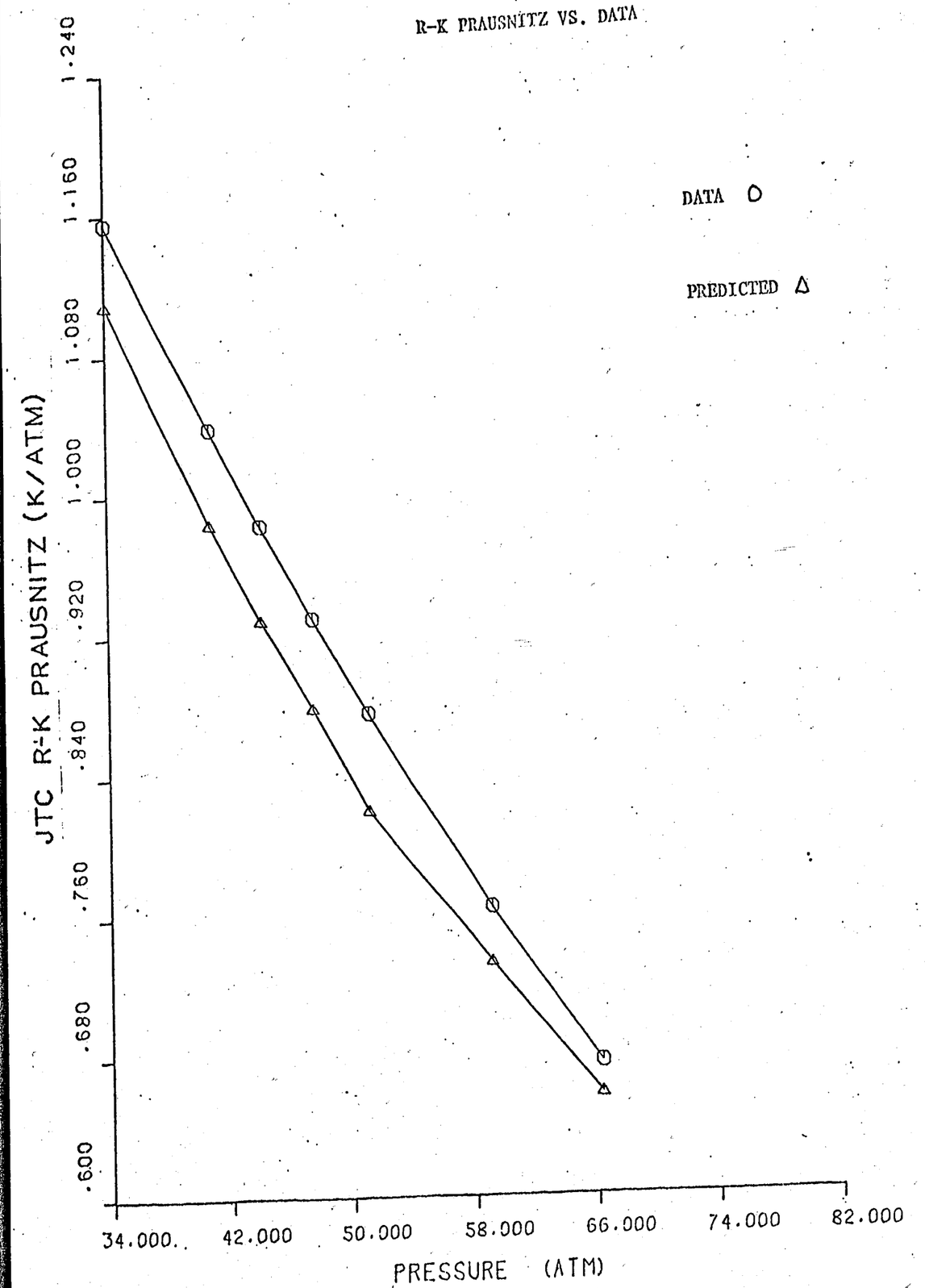
REDLICH-KWONG ORG. VS. DATA



RUN 1A

JOULE-THOMSON COEFFICIENTS

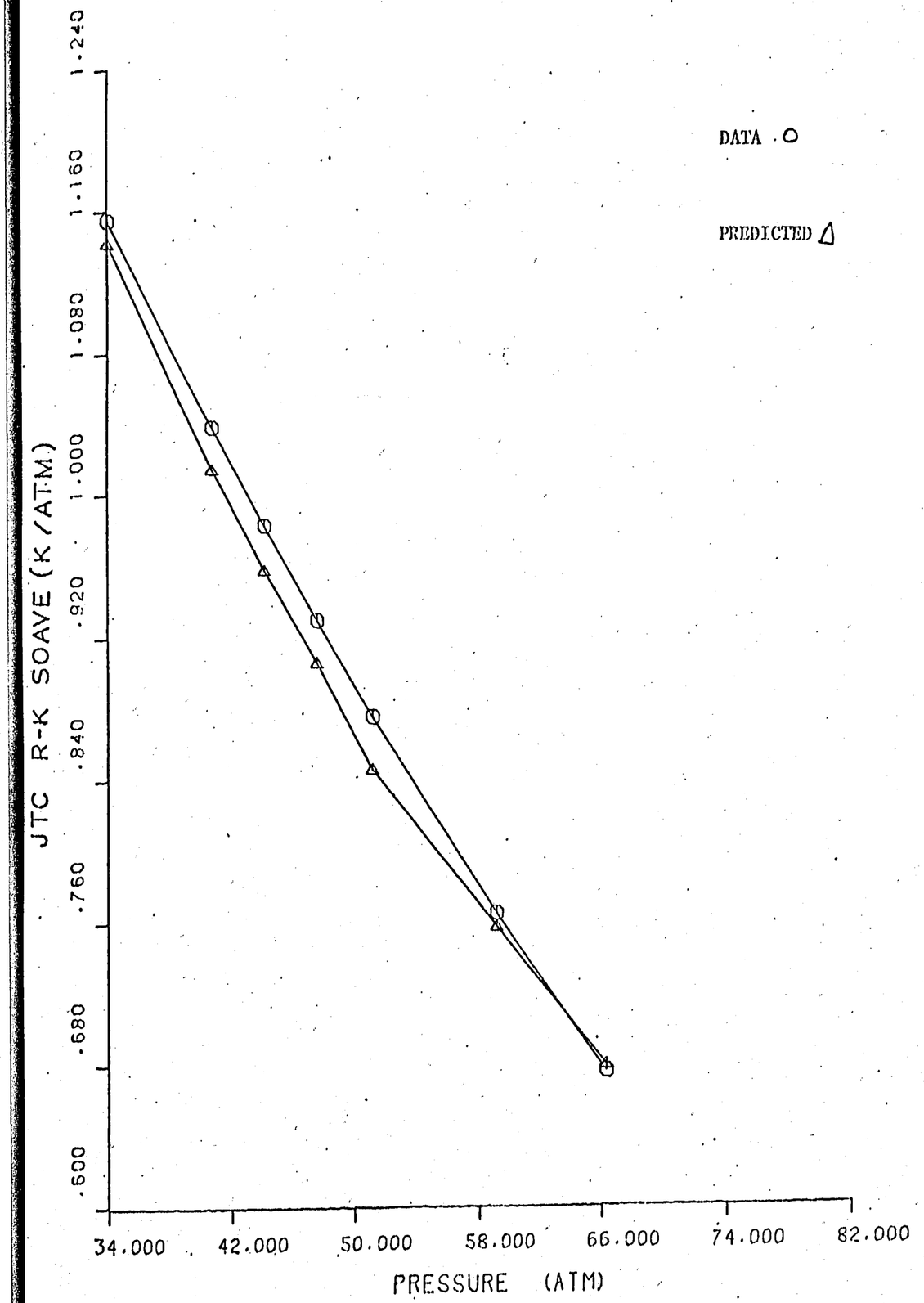
R-K PRAUSNITZ VS. DATA



RUN 1A

JOULE-THOMSON COEFFICIENTS

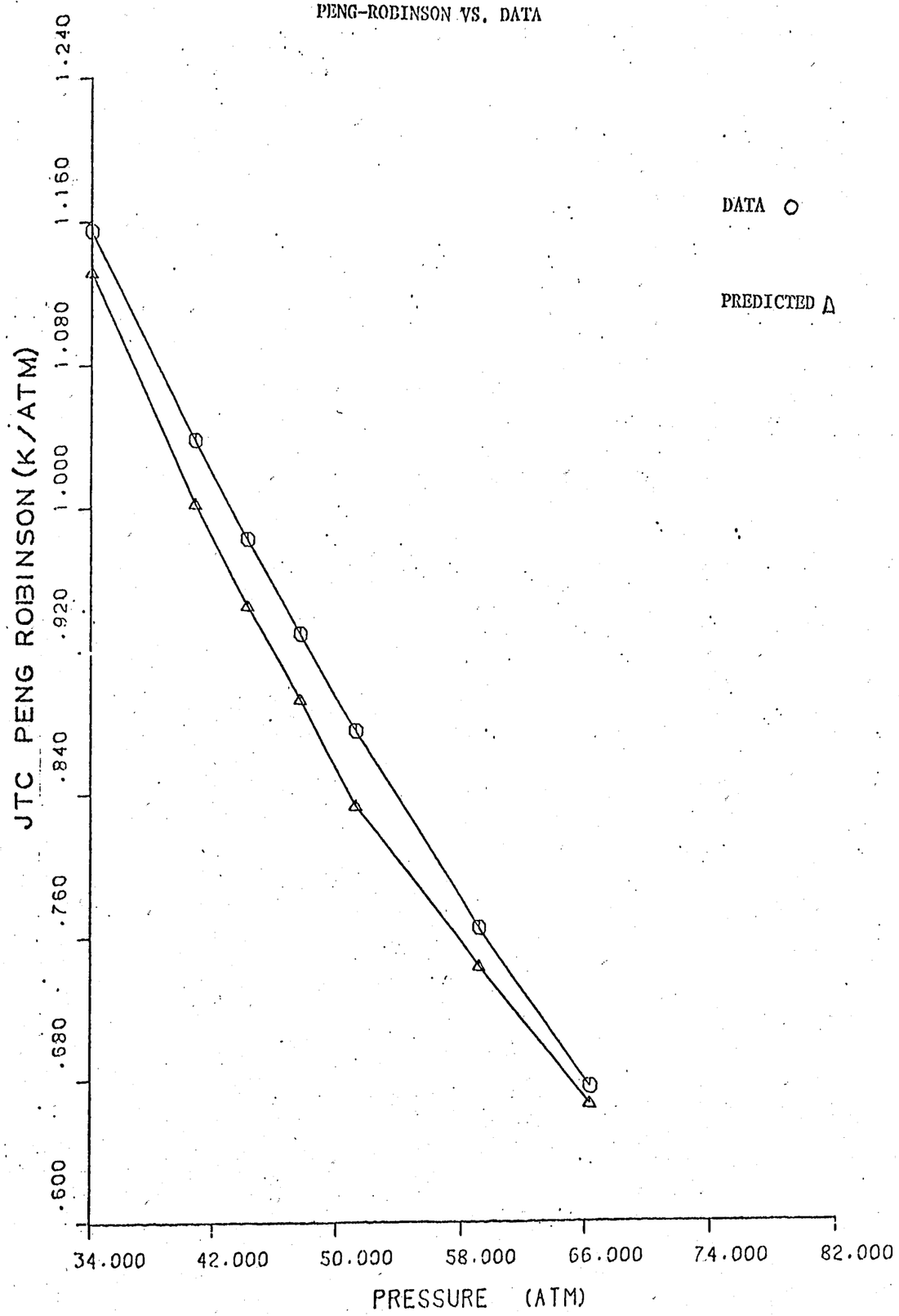
R-K SOAVE VS. DATA



RUN 1A

JOULE-THOMSON COEFFICIENTS

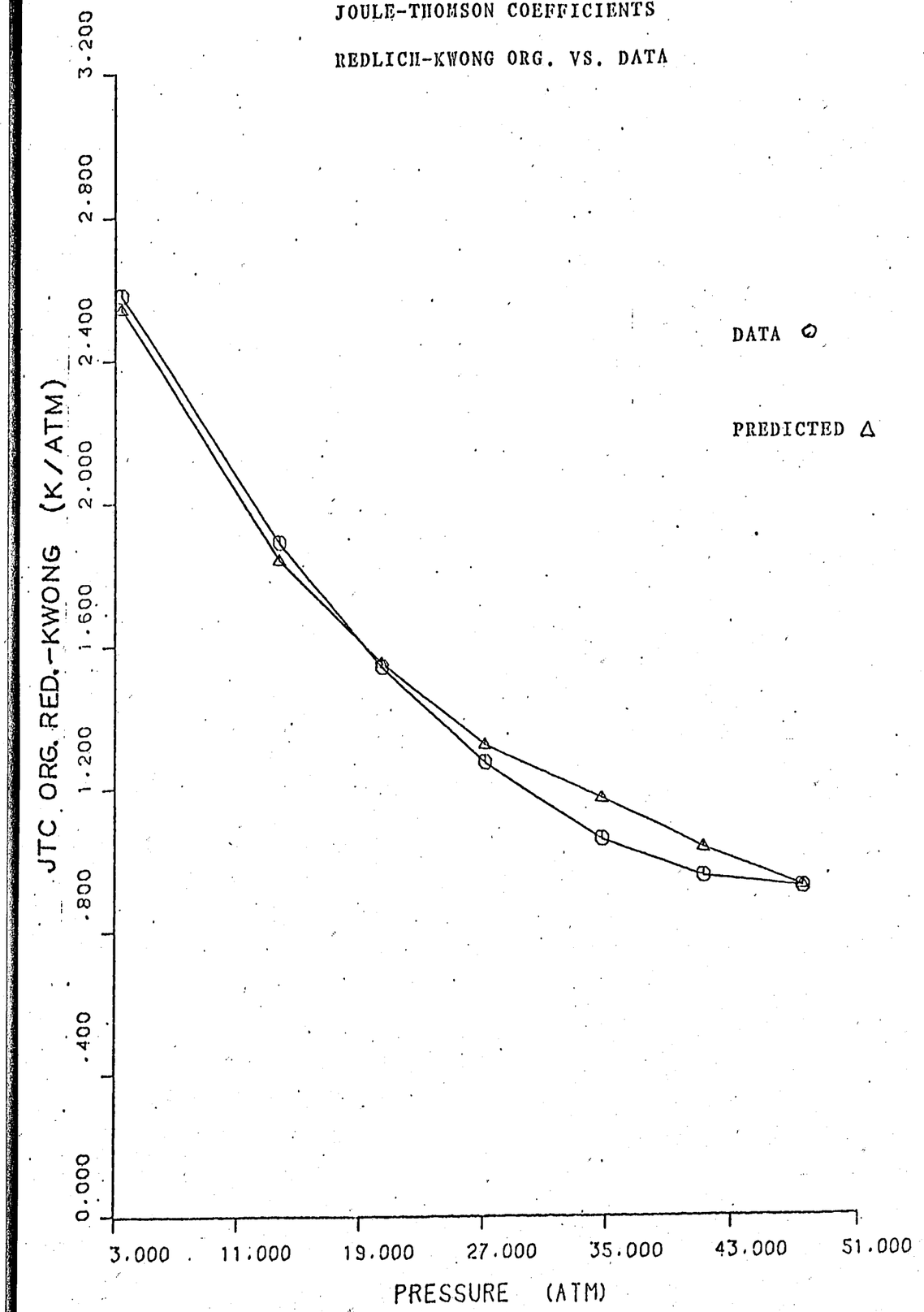
PENG-ROBINSON VS. DATA



RUN 1A

JOULE-THOMSON COEFFICIENTS

REDLICH-KWONG ORG. VS. DATA



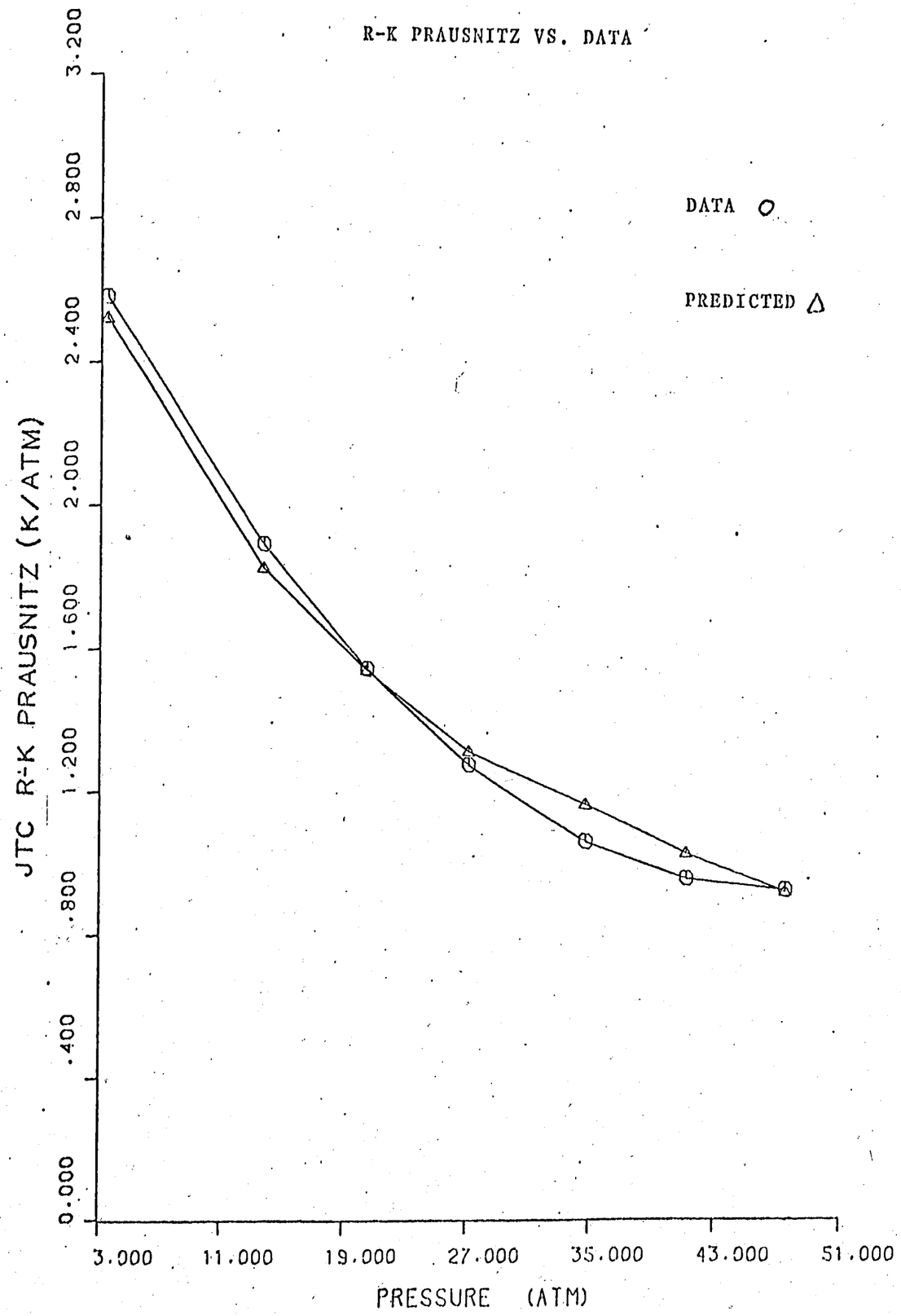
DATA ○

PREDICTED △

RUN 2A

JOULE-THOMSON COEFFICIENTS

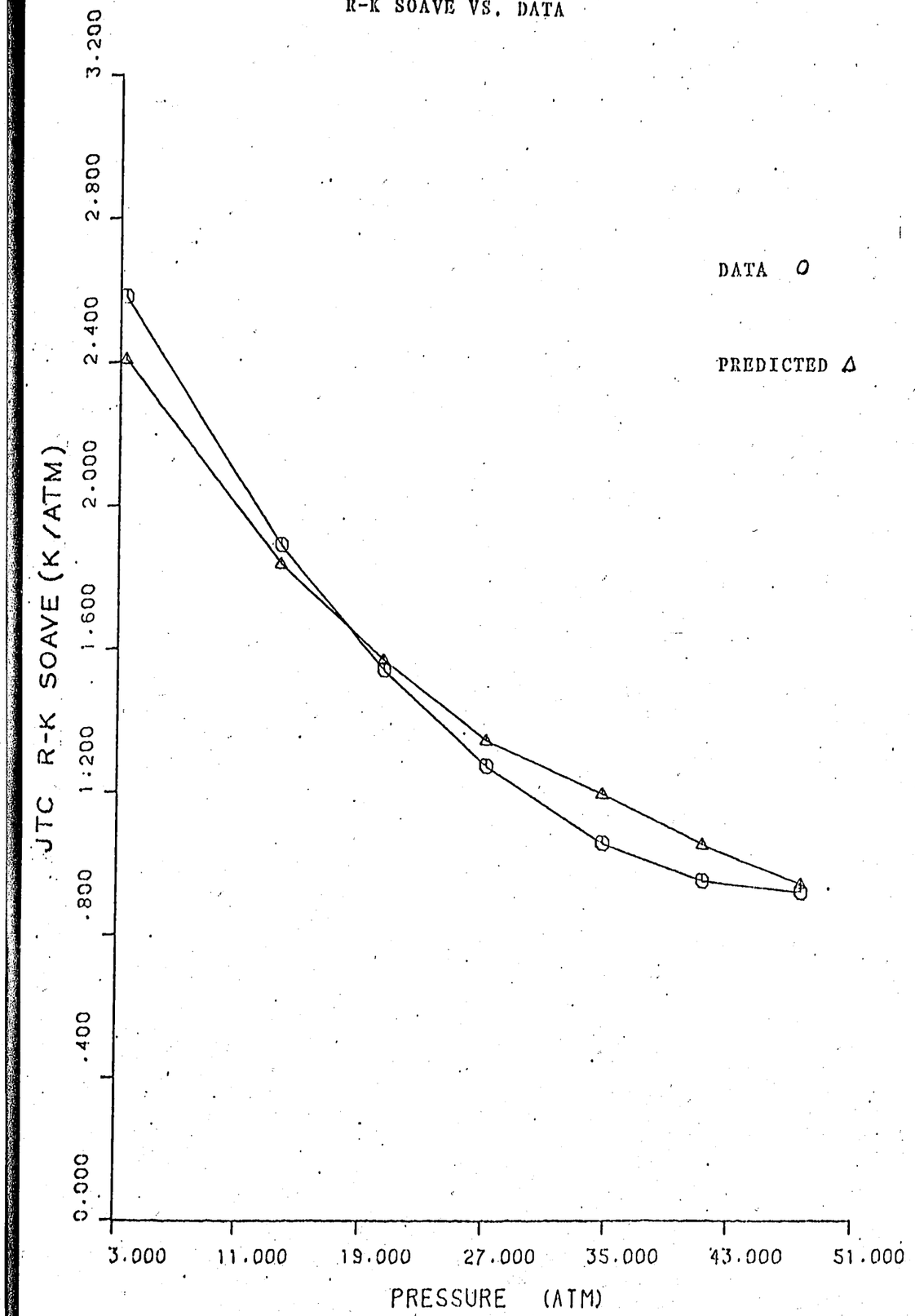
R-K PRAUSNITZ VS. DATA



RUN 2A

JOULE-THOMSON COEFFICIENTS

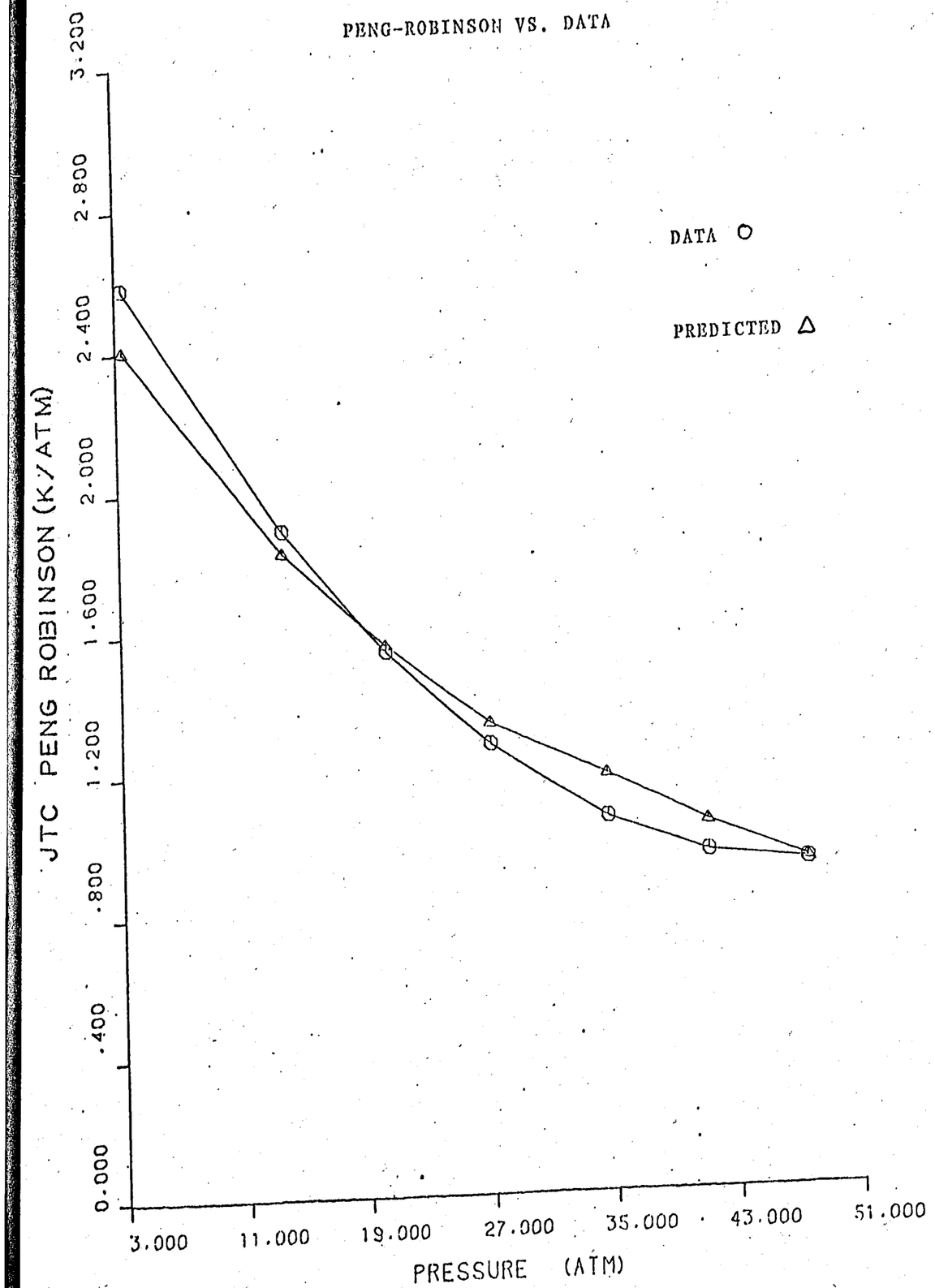
R-K SOAVE VS. DATA



RUN 2A

JOULE-THOMSON COEFFICIENTS

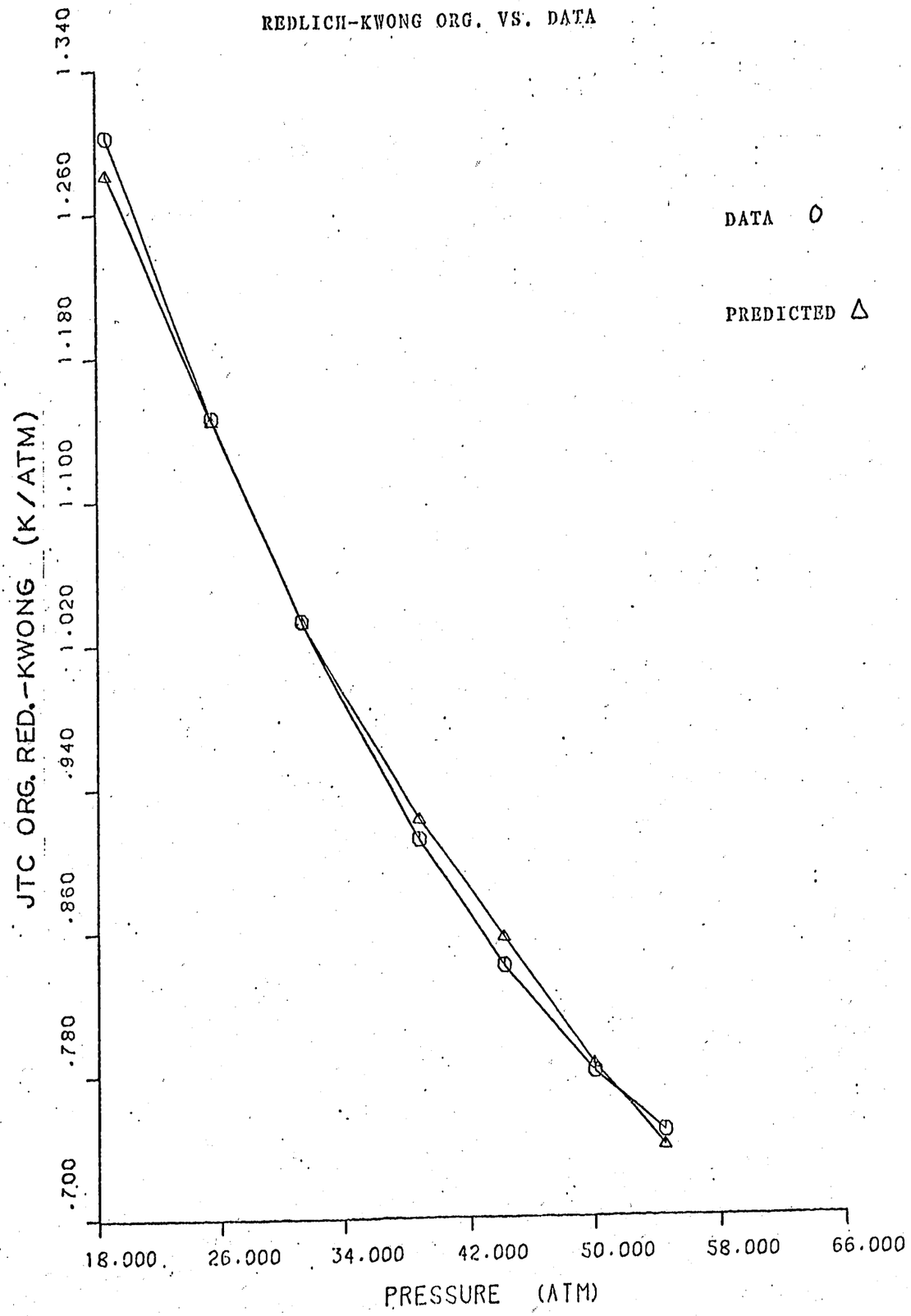
PENG-ROBINSON VS. DATA



RUN 2A

JOULE-THOMSON COEFFICIENTS

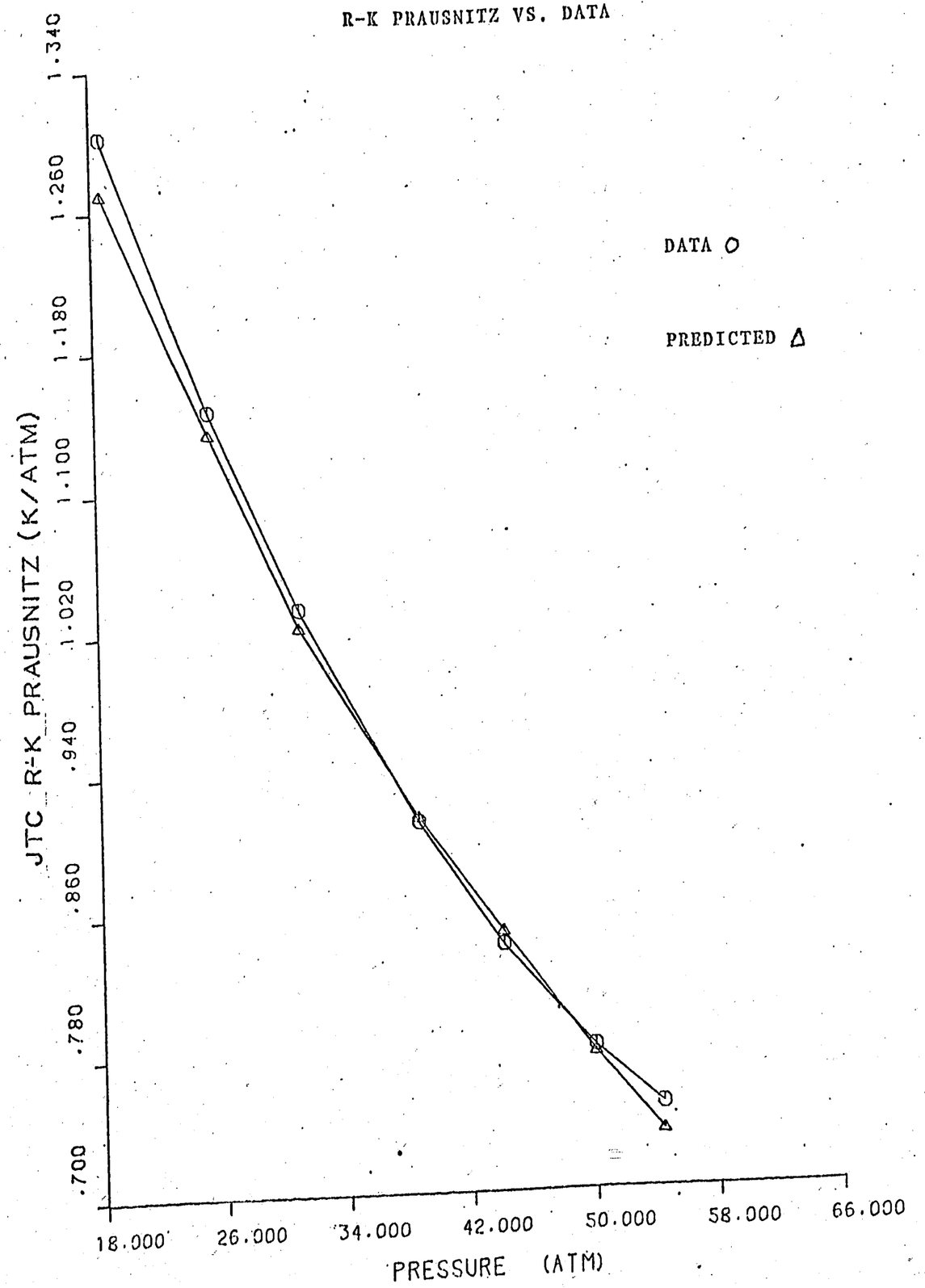
REDLICH-KWONG ORG. VS. DATA



RUN 3A

JOULE-THOMSON COEFFICIENTS

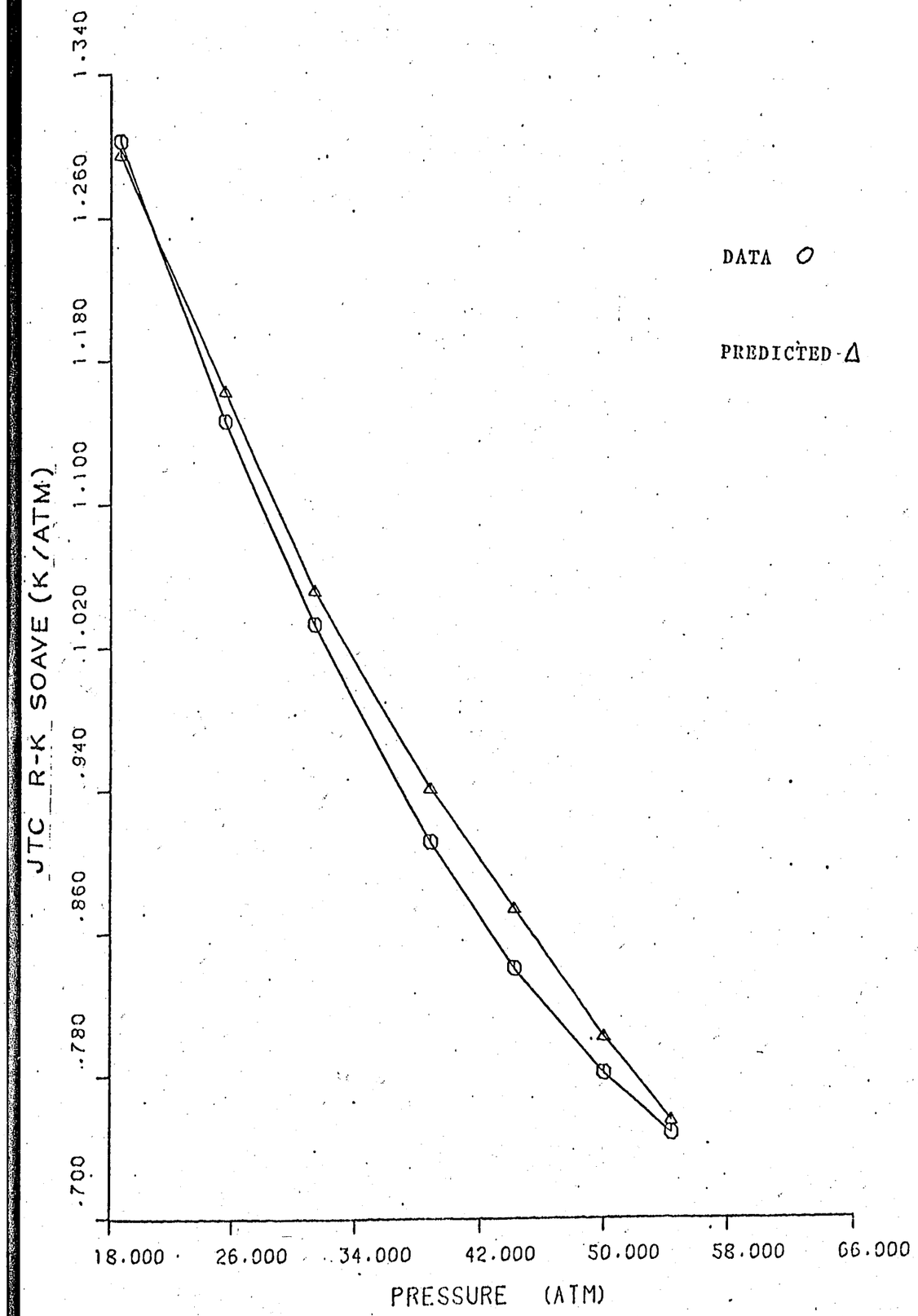
R-K PRAUSNITZ VS. DATA



RUN 3A

JOULE-THOMSON COEFFICIENTS

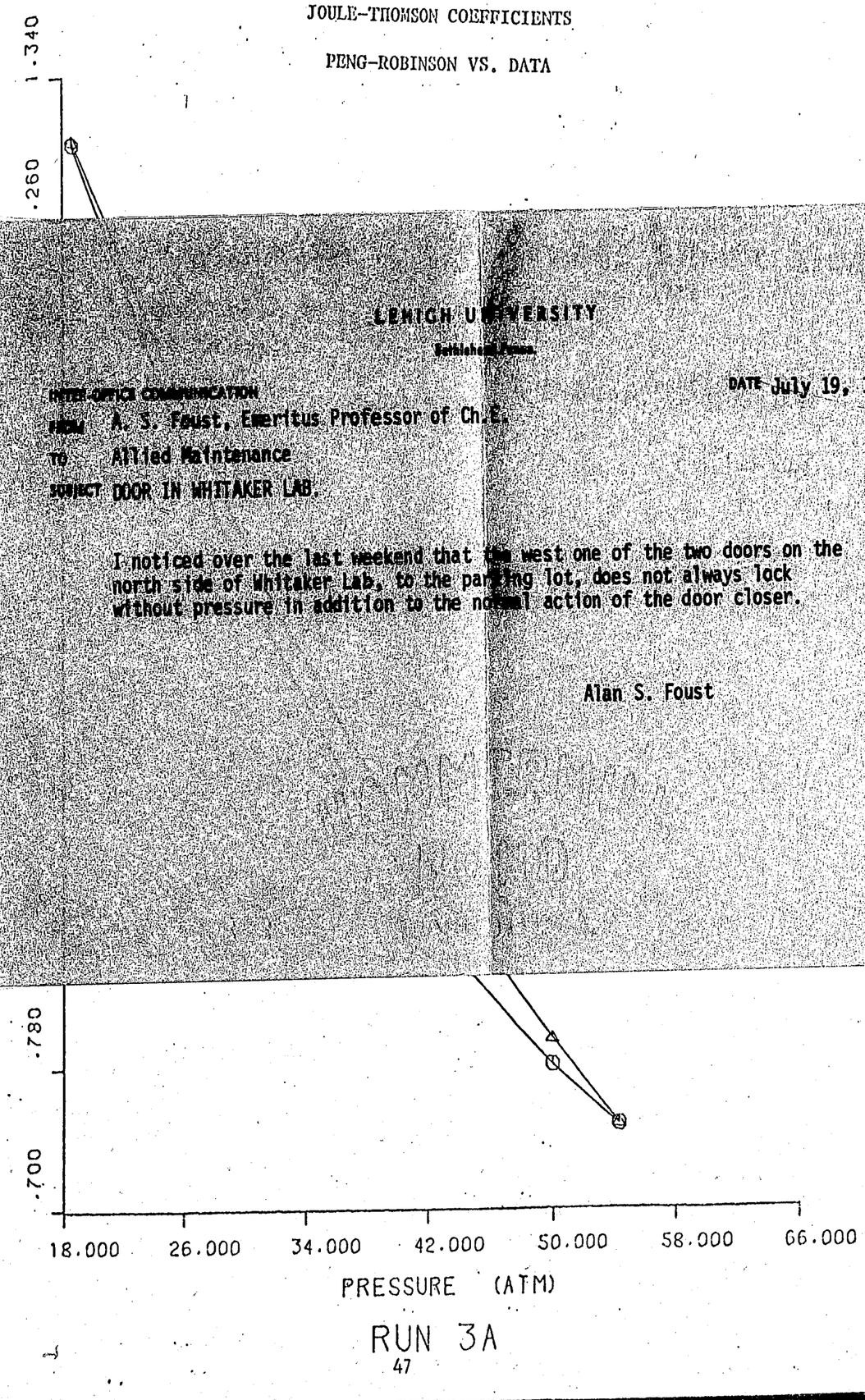
R-K SOAVE VS. DATA



RUN 3A

JOULE-THOMSON COEFFICIENTS

PENG-ROBINSON VS. DATA



LEHIGH UNIVERSITY

Bethlehem, Penna.

INTER-OFFICE COMMUNICATION

DATE July 19, 1983

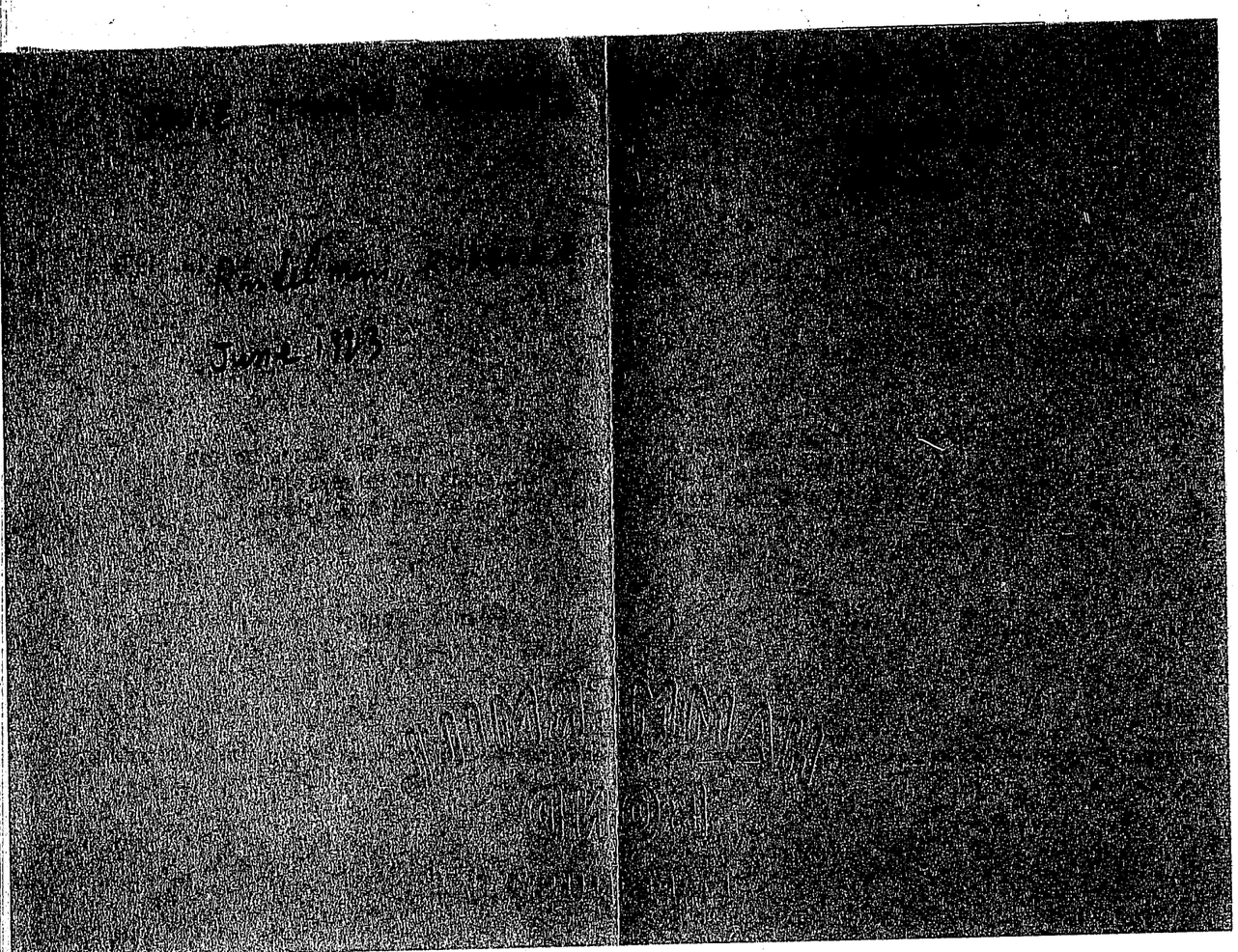
FROM A. S. Faust, Emeritus Professor of Ch.E.

TO Allied Maintenance

SUBJECT DOOR IN WHITAKER LAB.

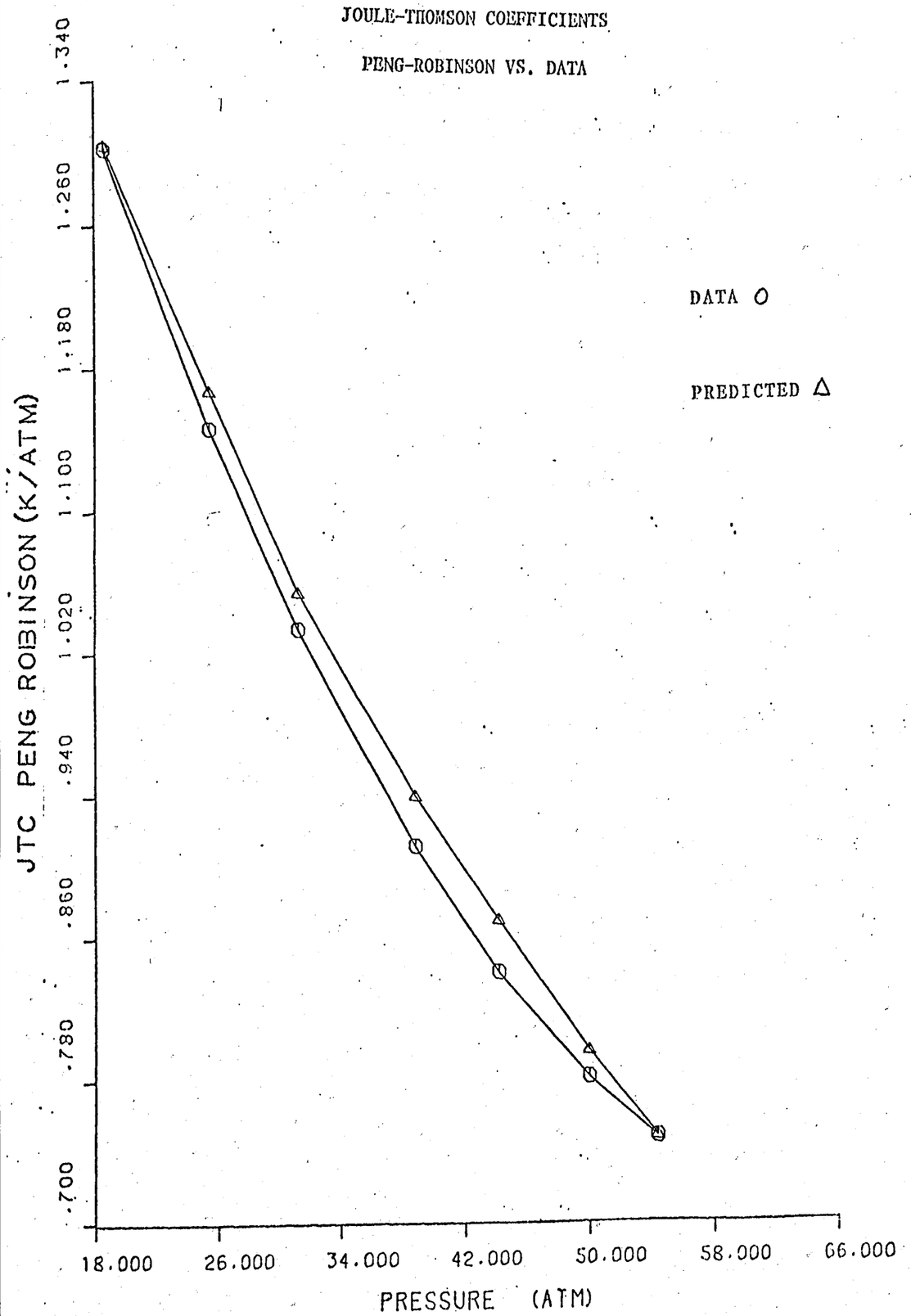
I noticed over the last weekend that the west one of the two doors on the north side of Whitaker Lab, to the parking lot, does not always lock without pressure in addition to the normal action of the door closer.

Alan S. Foust



JOULE-THOMSON COEFFICIENTS

PENG-ROBINSON VS. DATA



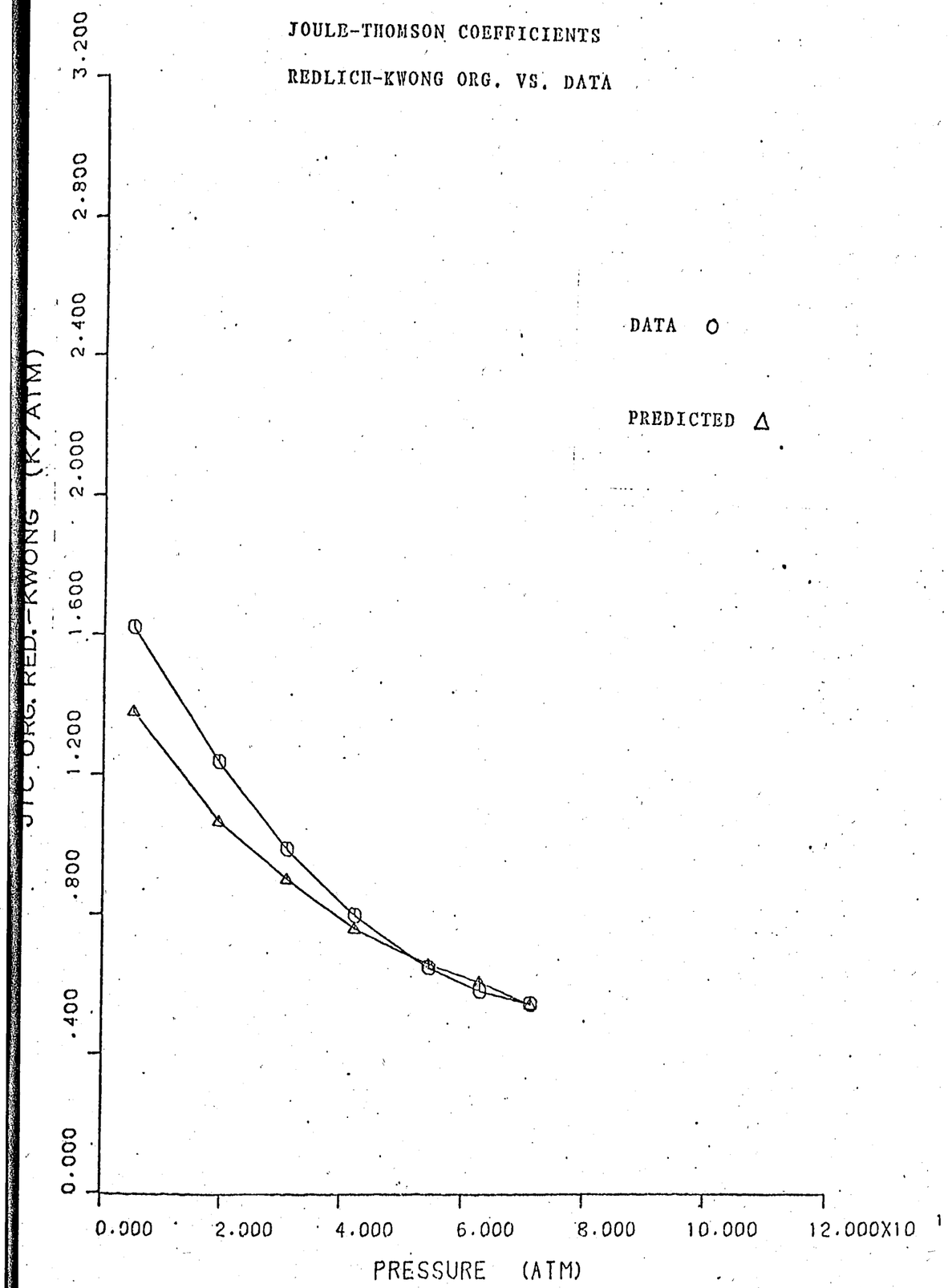
DATA O

PREDICTED Δ

RUN 3A

JOULE-THOMSON COEFFICIENTS

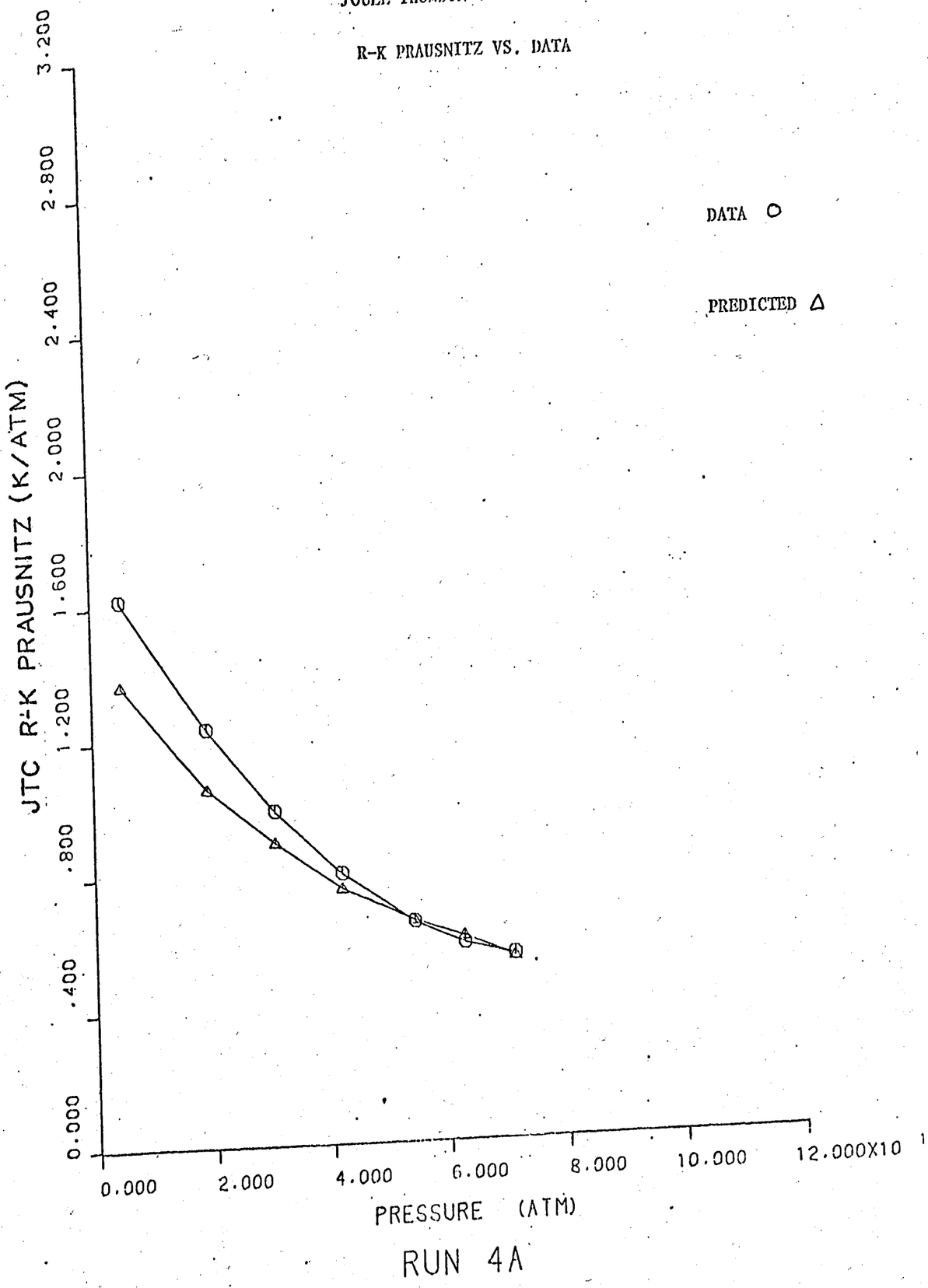
REDLICH-KWONG ORG. VS. DATA



RUN 4A

JOULE-THOMSON COEFFICIENTS

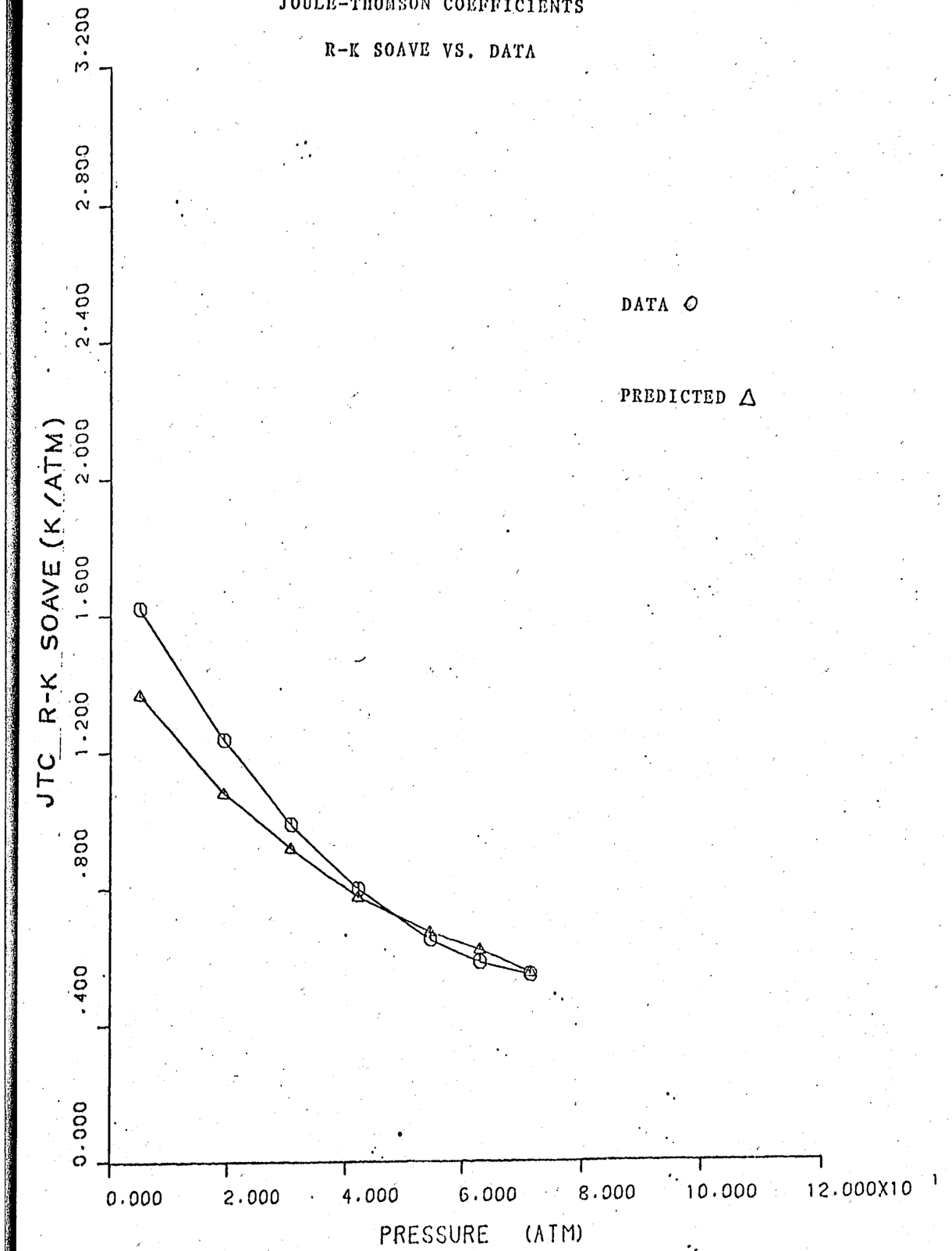
R-K PRAUSNITZ VS. DATA



RUN 4A

JOULE-THOMSON COEFFICIENTS

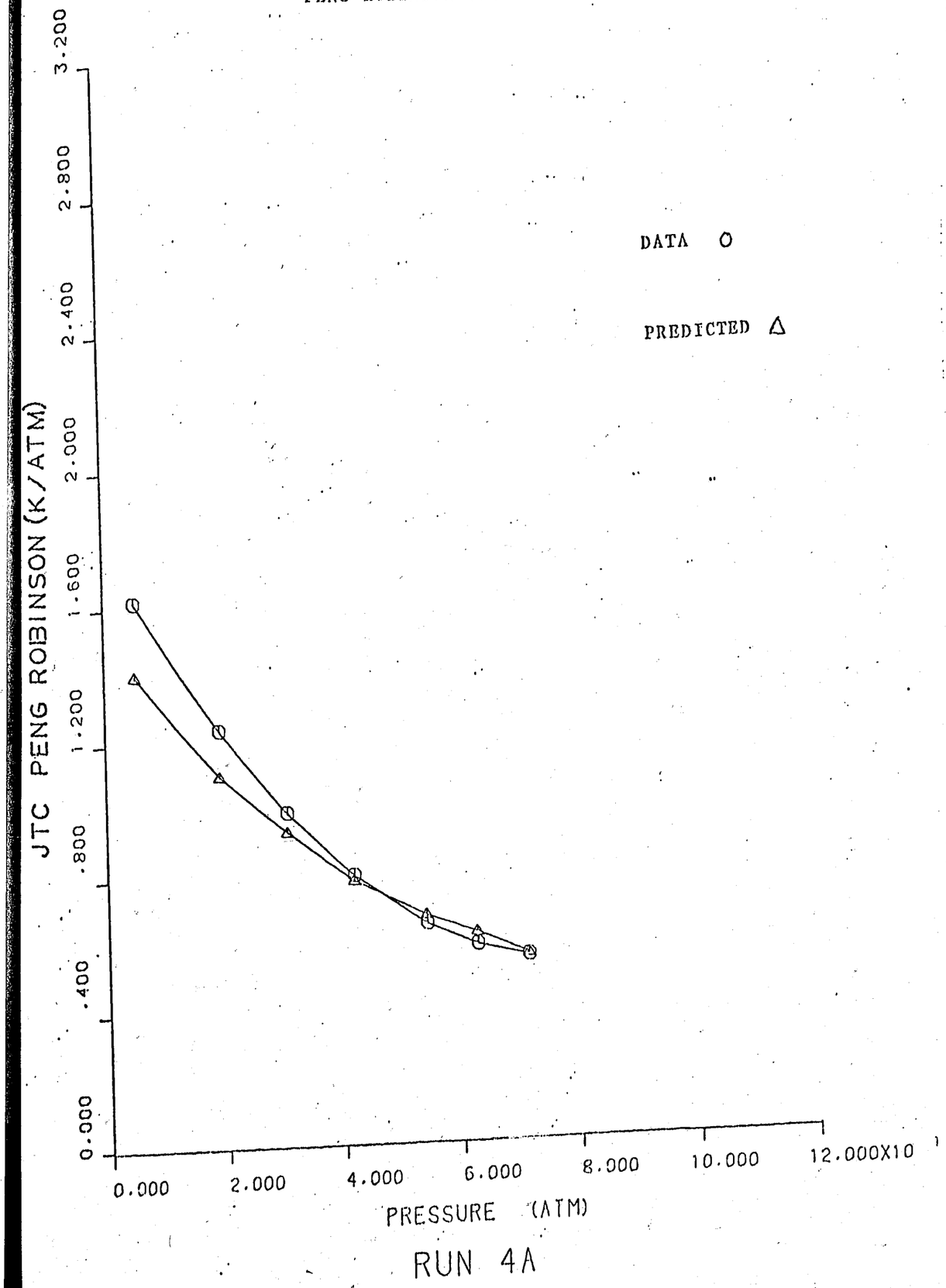
R-K SOAVE VS. DATA



RUN 4A

JOULE-THOMSON COEFFICIENTS

PENG-ROBINSON VS. DATA

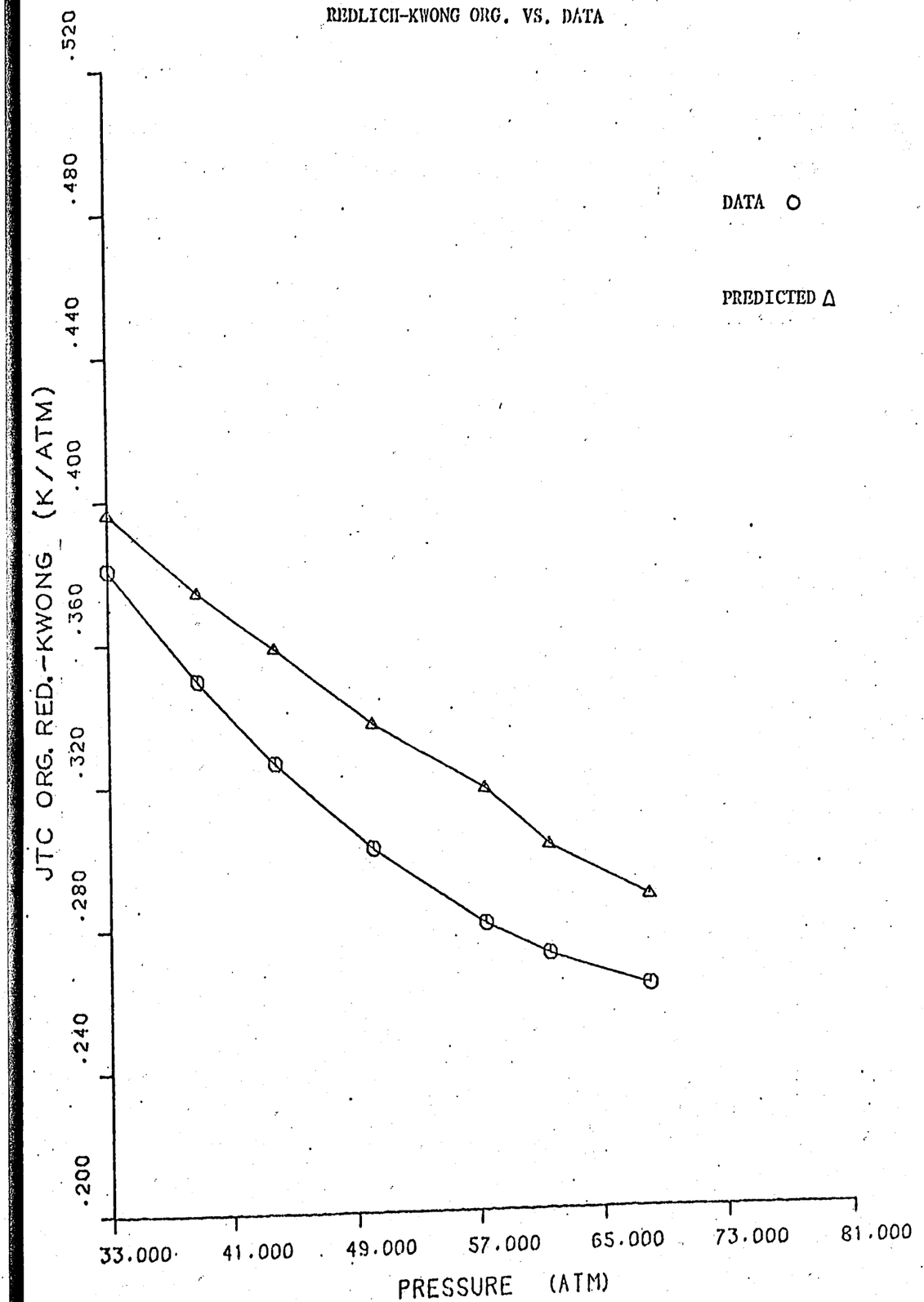


RUN 4A

Figure 7-3: MIXTURE B COEFFICIENTS: DATA vs.PREDICTED

JOULE-THOMSON COEFFICIENTS

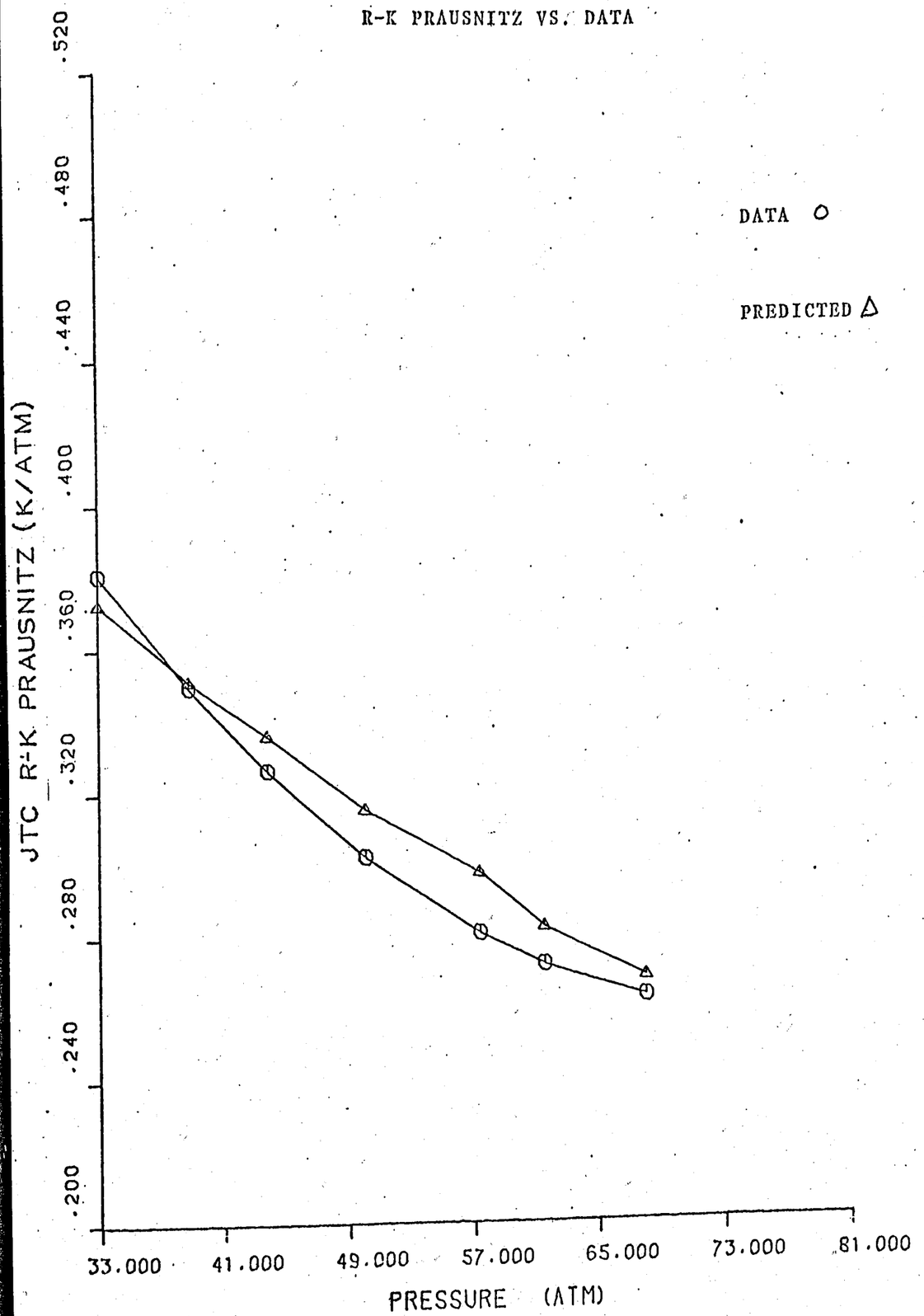
REDLICH-KWONG ORG. VS. DATA



RUN 1B

JOULE-THOMSON COEFFICIENTS

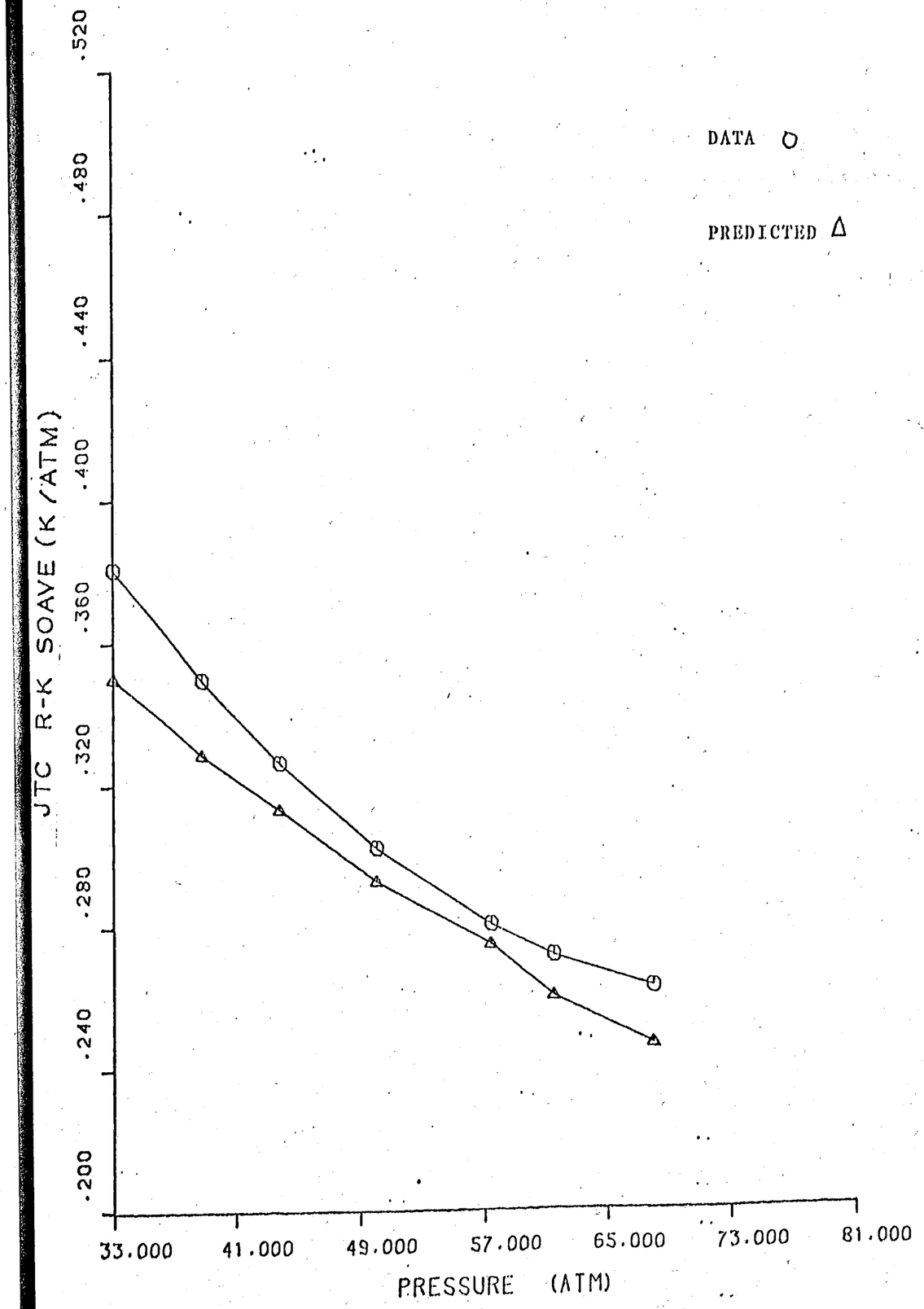
R-K PRAUSNITZ VS. DATA



RUN 1B

JOULE-THOMSON COEFFICIENTS

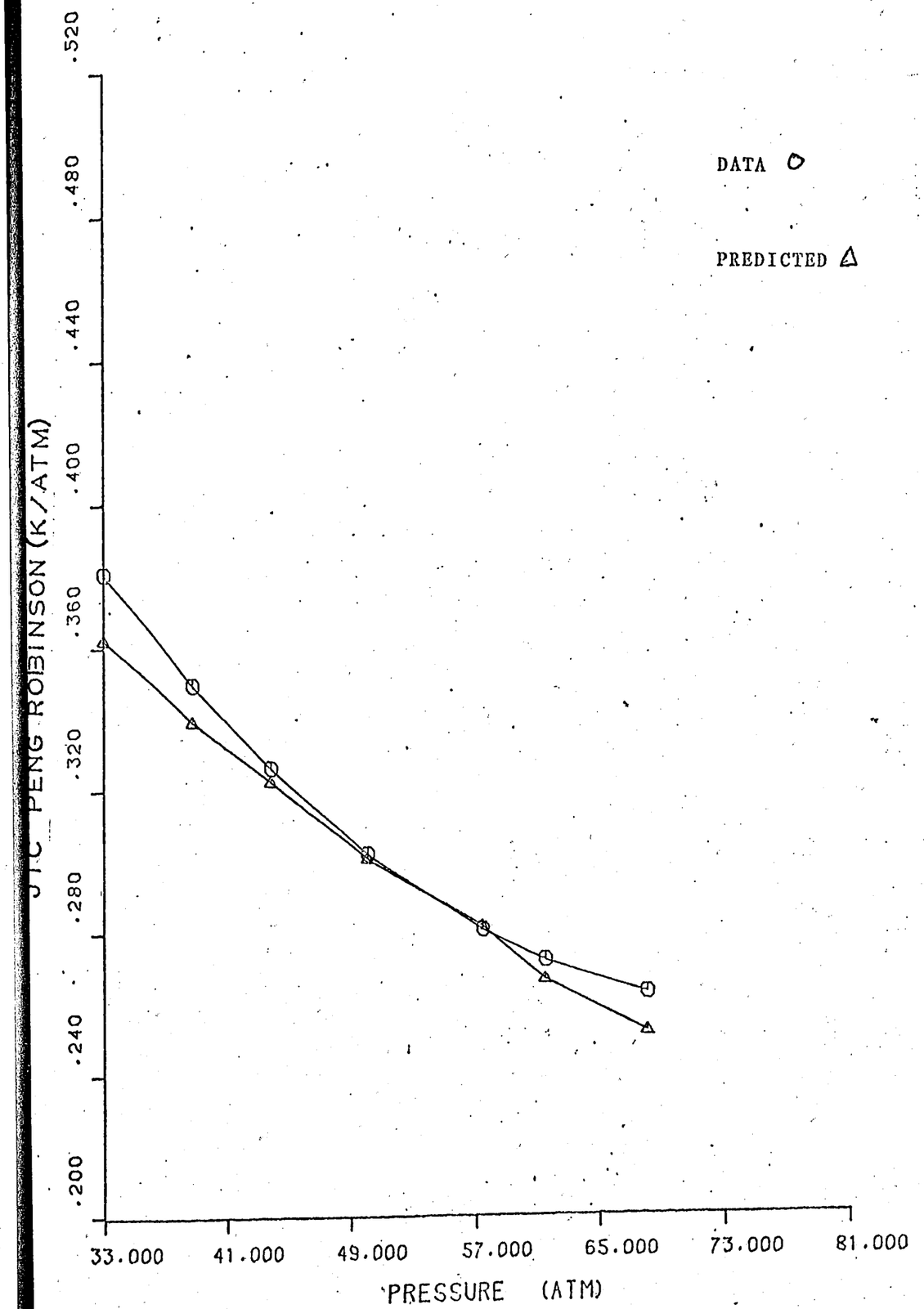
R-K SOAVE VS. DATA



RUN 1B

JOULE-THOMSON COEFFICIENTS

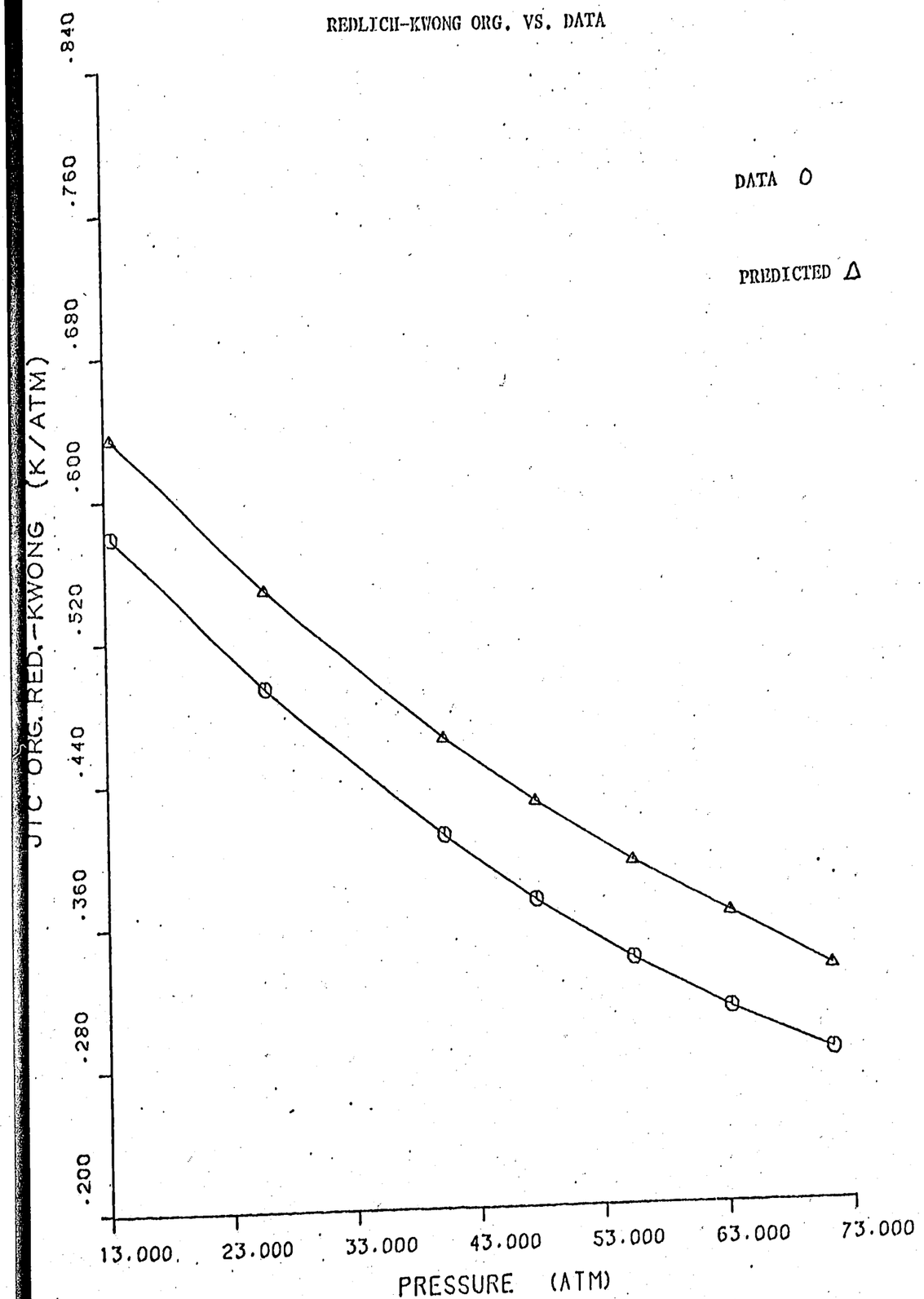
PENG-ROBINSON VS. DATA



RUN 1B

JOULE-THOMSON COEFFICIENTS

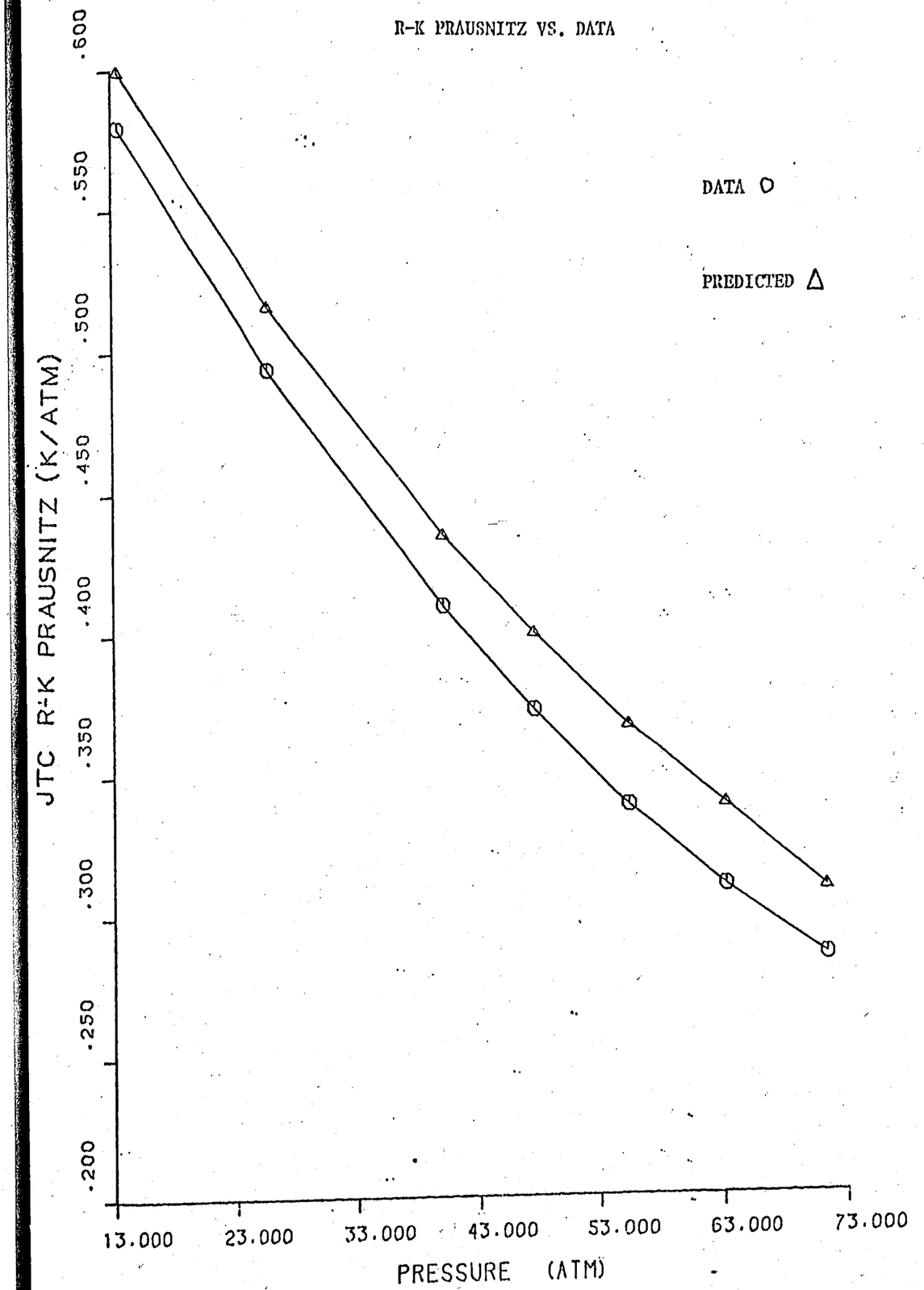
REDLICH-KWONG ORG. VS. DATA



RUN 2B

JOULE-THOMSON COEFFICIENTS

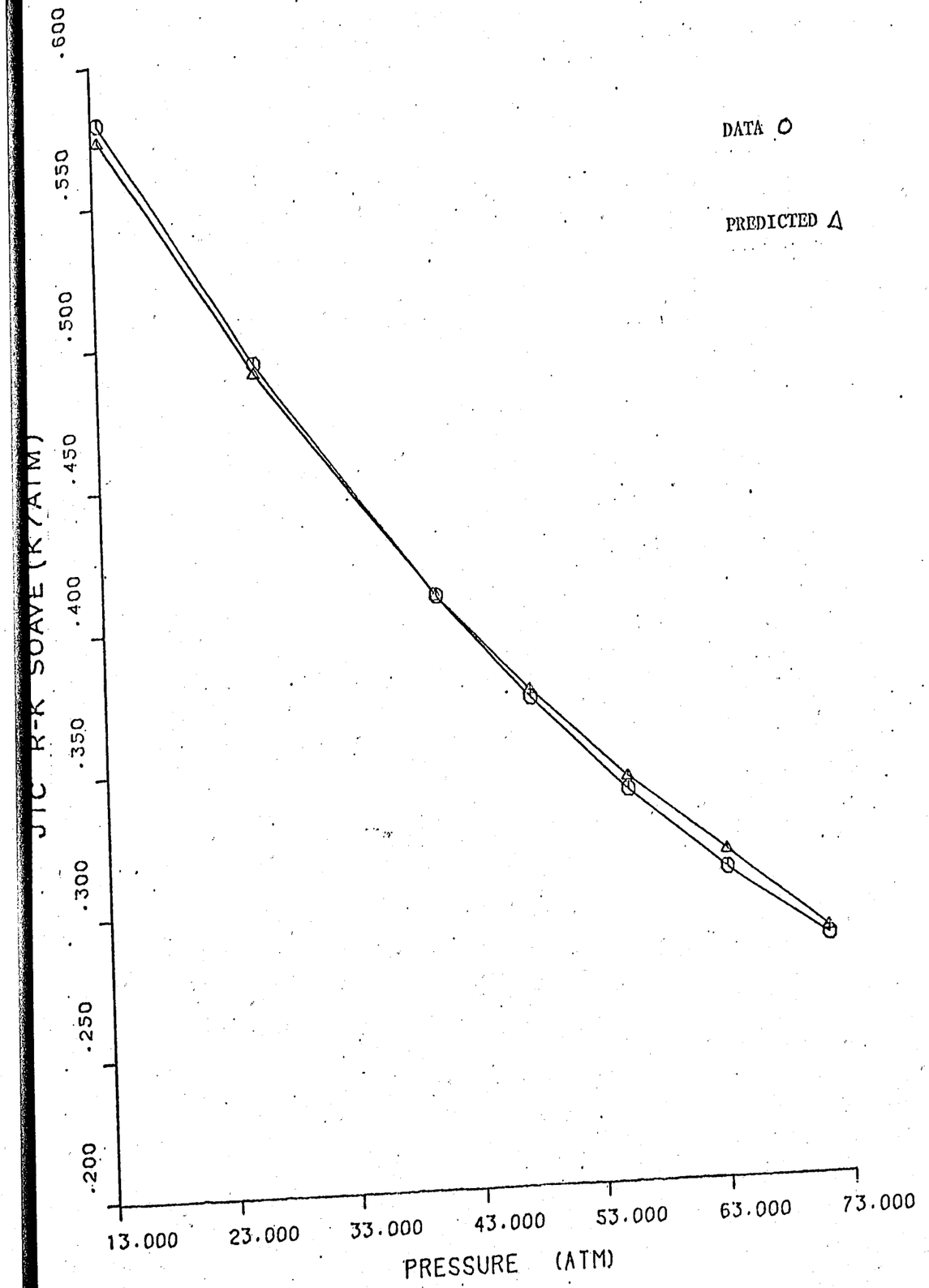
R-K PRAUSNITZ VS. DATA



RUN 2B

JOULE-THOMSON COEFFICIENTS

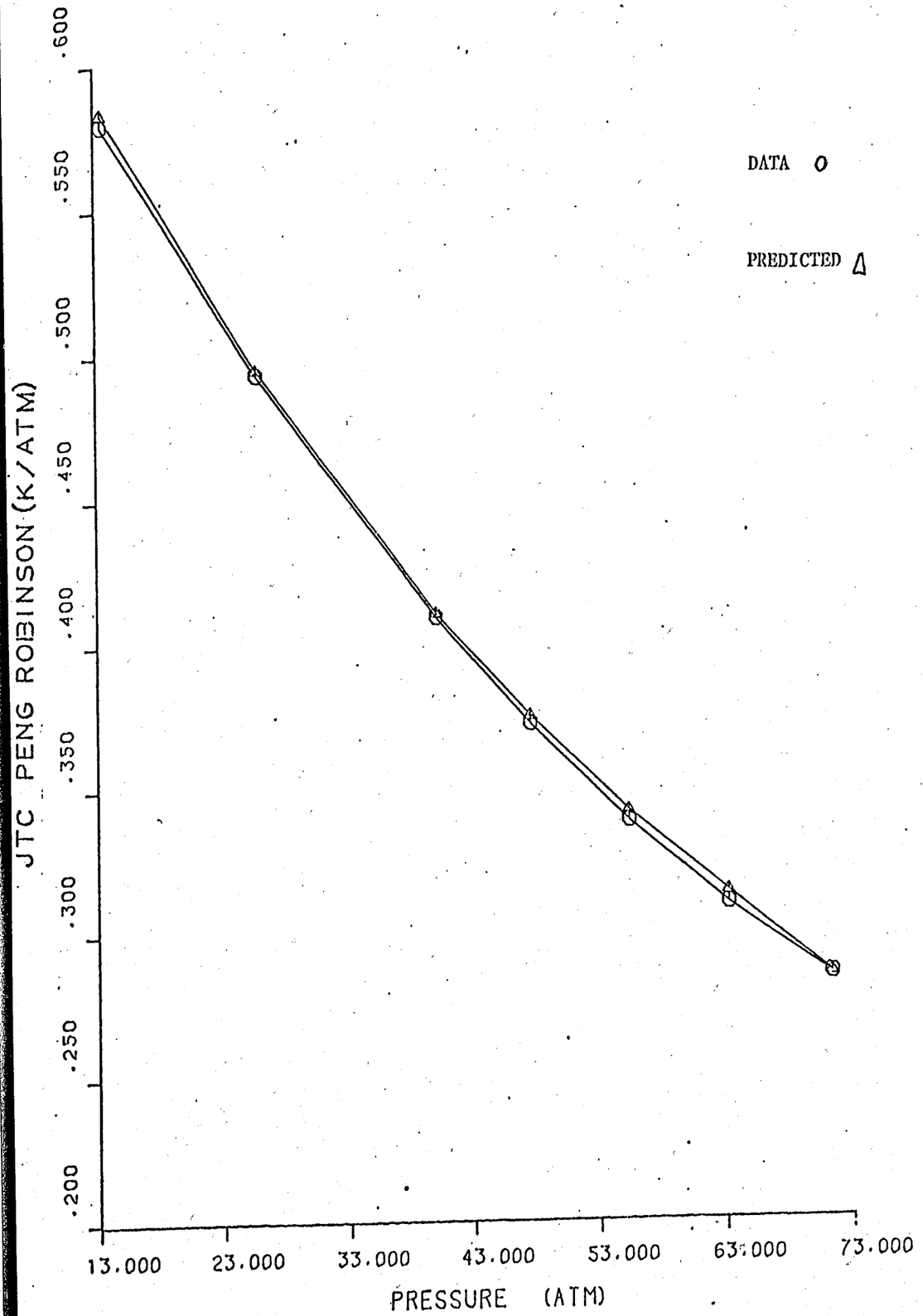
R-K SOAVE VS. DATA



RUN 2B

JOULE-THOMSON COEFFICIENTS

PENG-ROBINSON VS. DATA



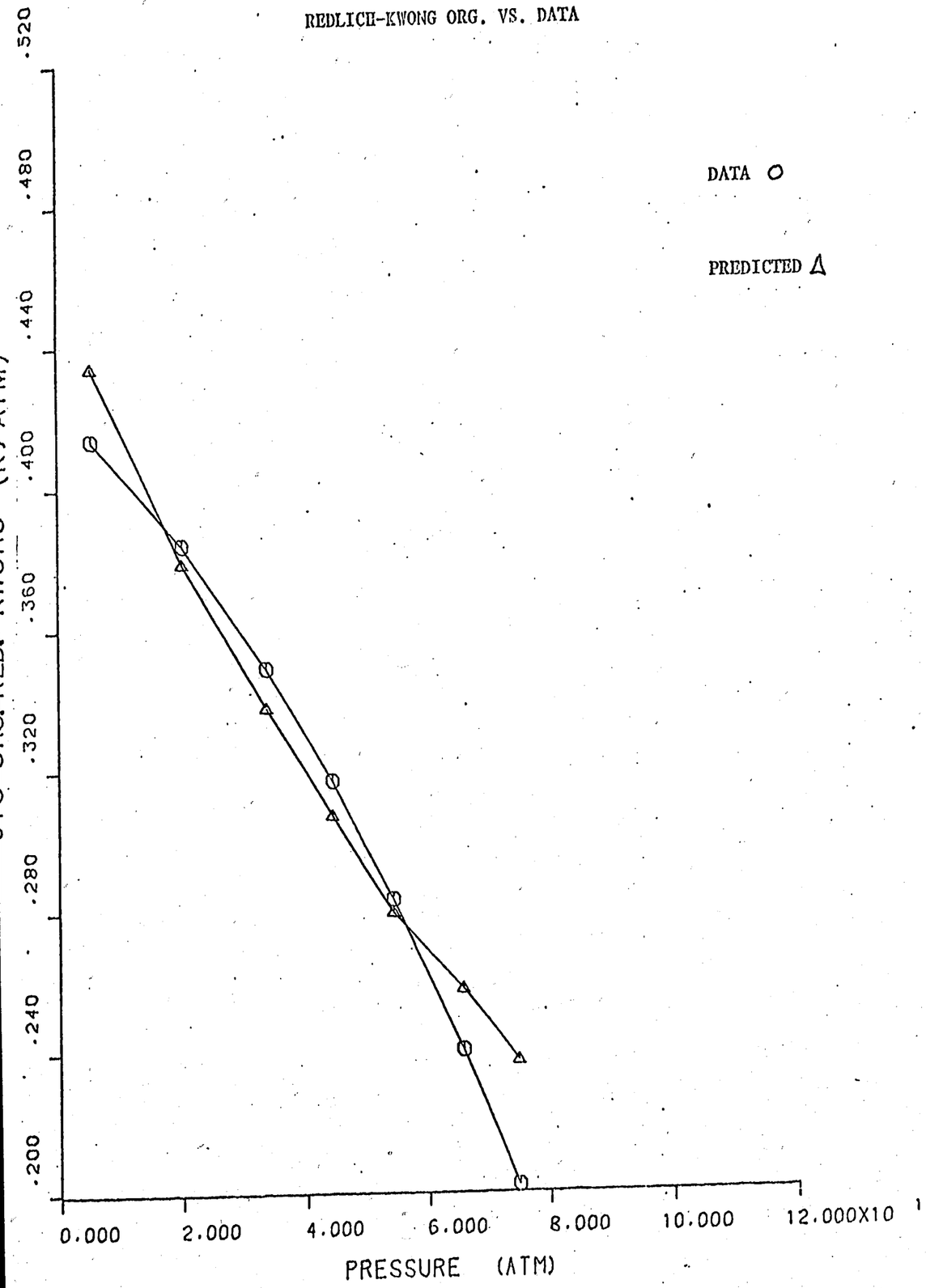
DATA o

PREDICTED Δ

RUN 2B

JOULE-THOMSON COEFFICIENTS

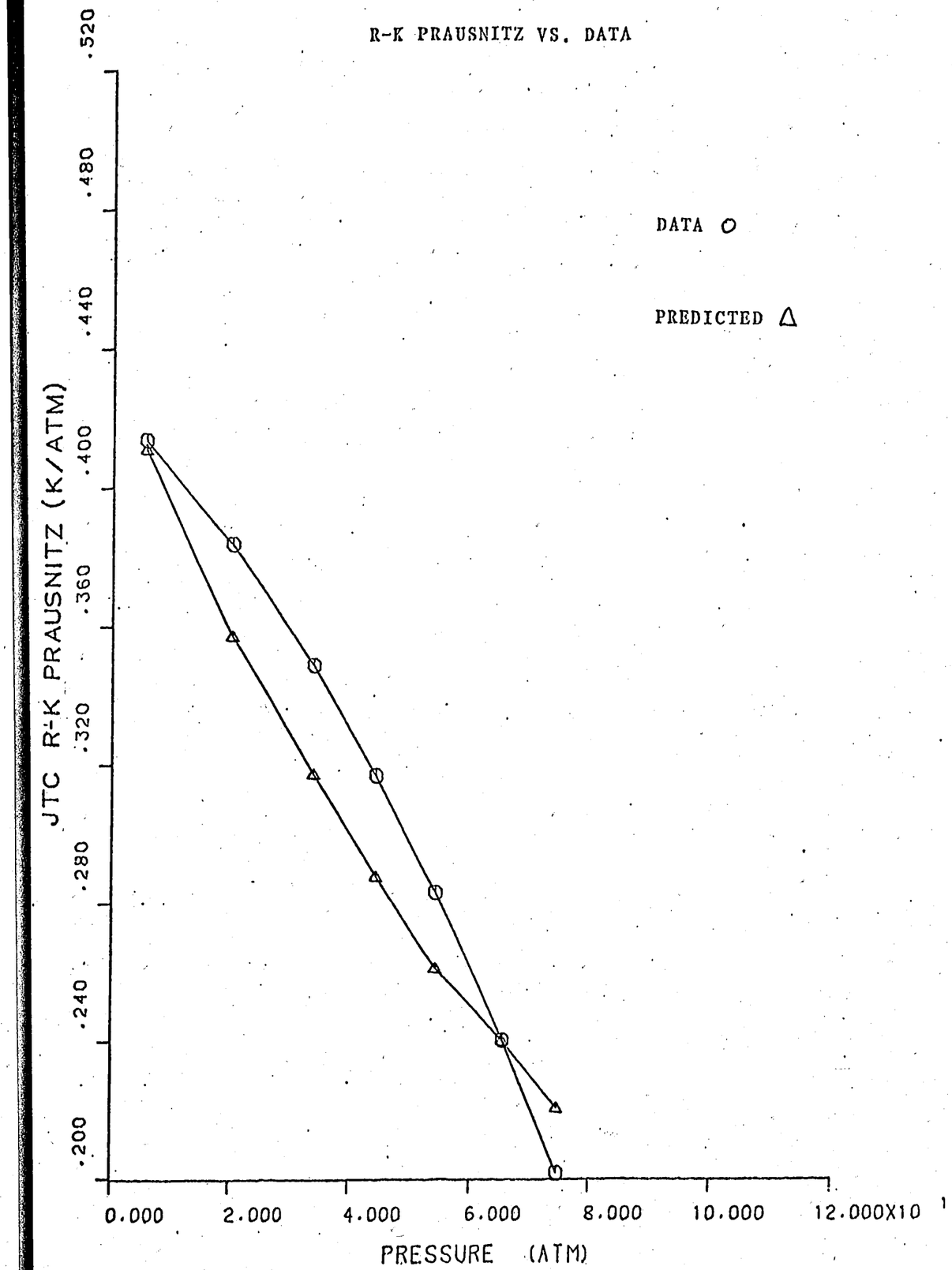
REDLICH-KWONG ORG. VS. DATA



RUN 3B

JOULE-THOMSON COEFFICIENTS

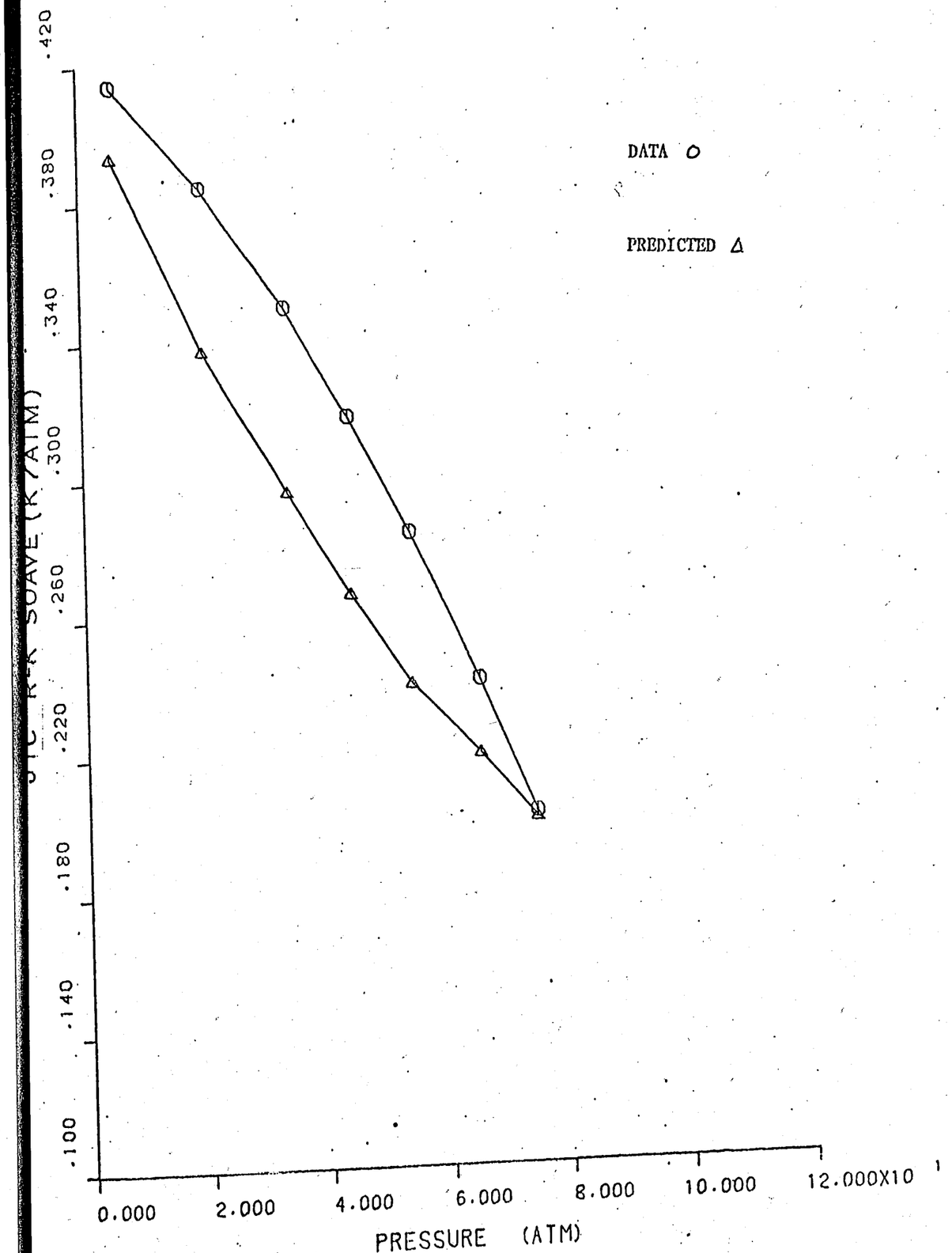
R-K PRAUSNITZ VS. DATA



RUN 3B

JOULE-THOMSON COEFFICIENTS

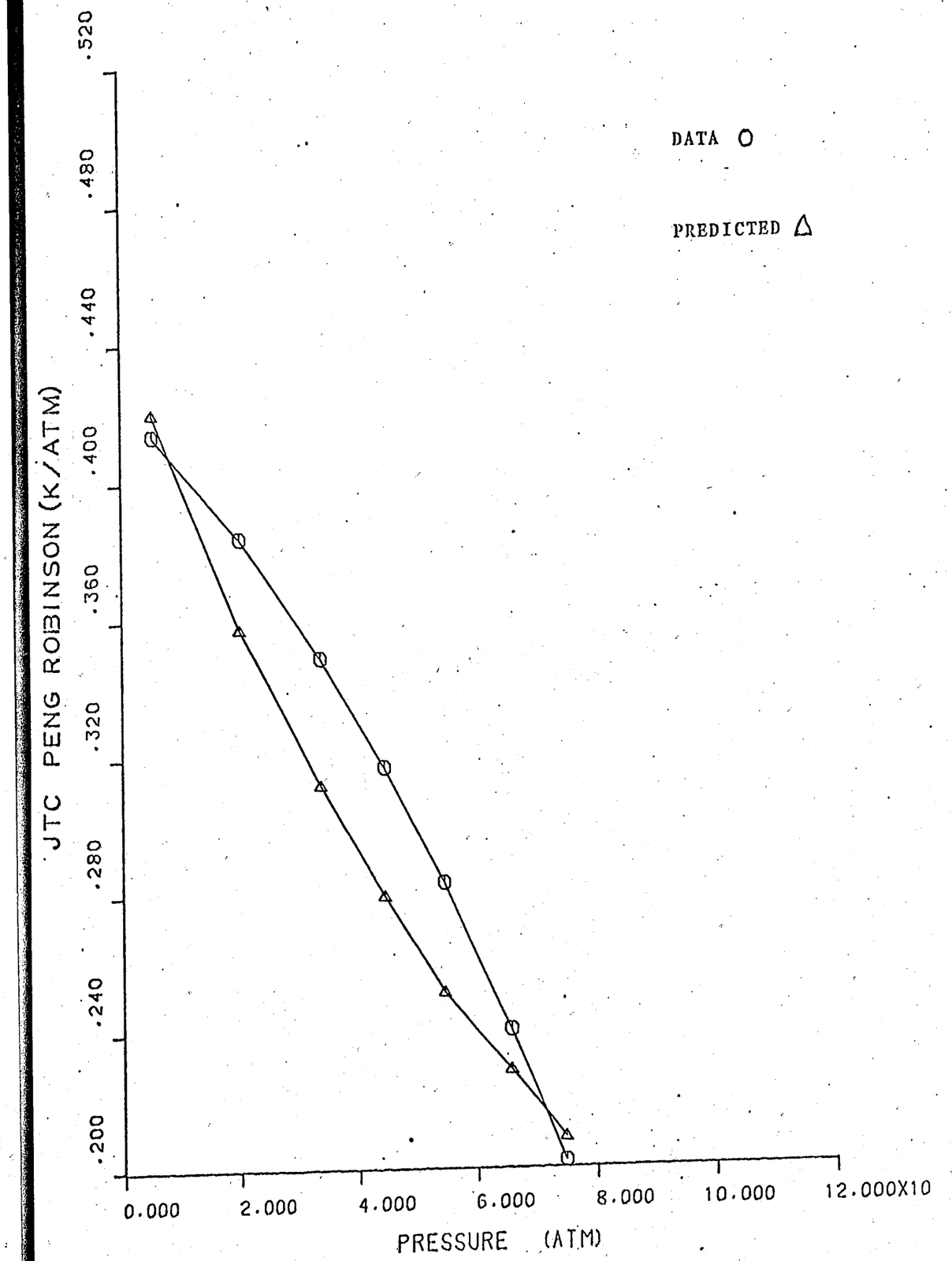
R-K SOAVE VS. DATA



RUN 3B

JOULE-THOMSON COEFFICIENTS

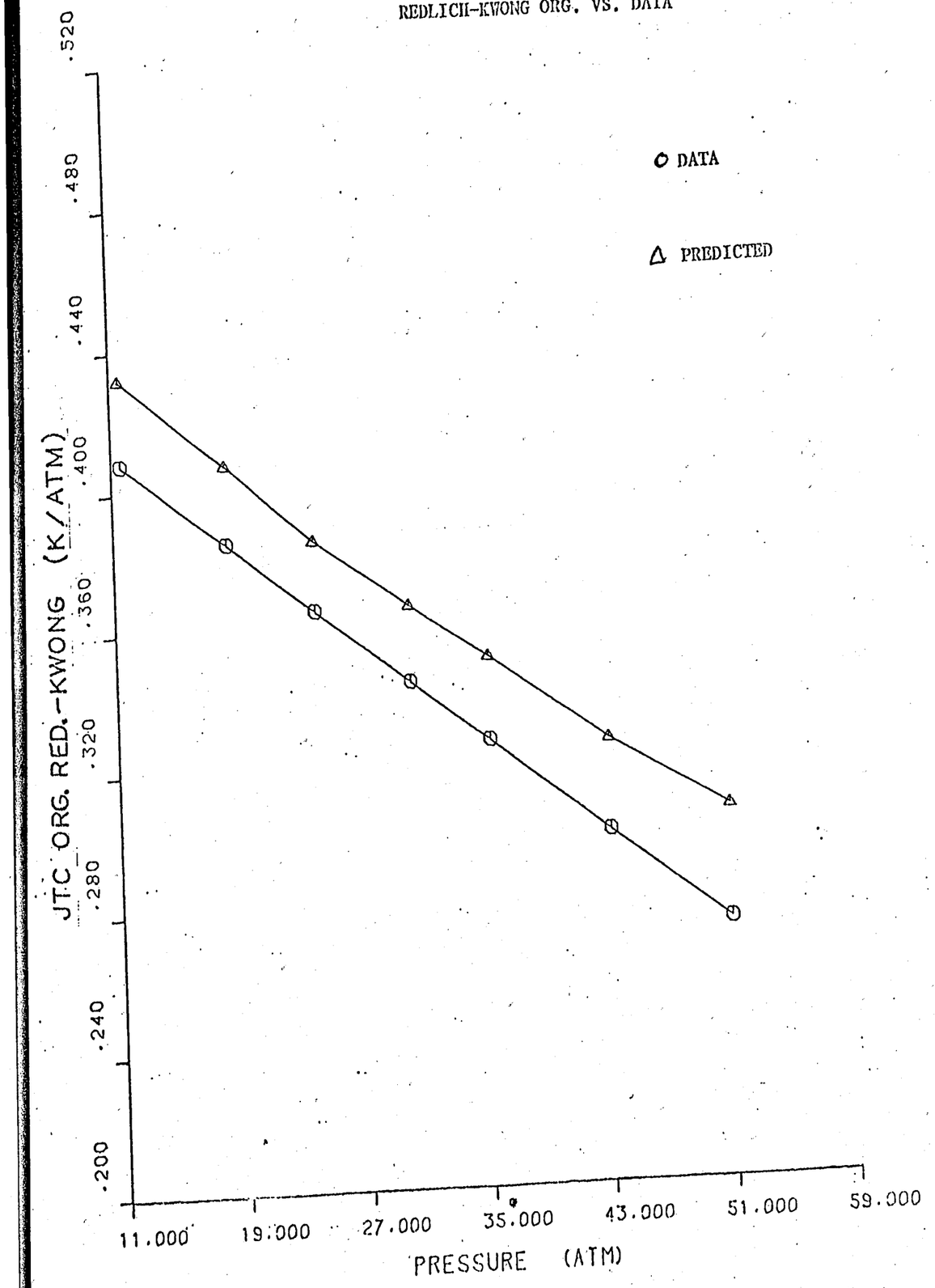
PENG-ROBINSON VS. DATA



RUN 3B

JOULE-THOMSON COEFFICIENTS

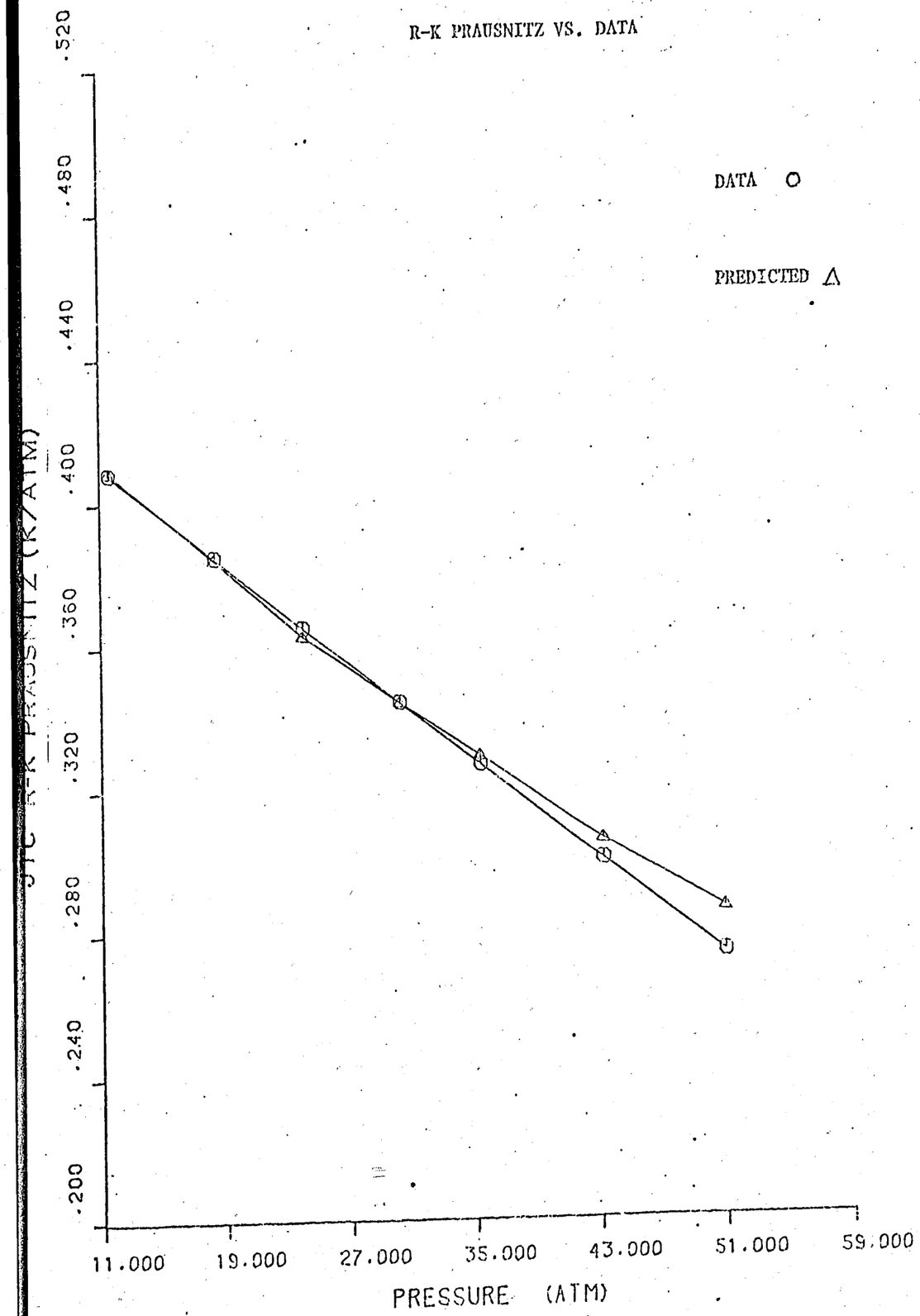
REDLICH-KWONG ORG. VS. DATA



RUN 4B

JOULE-THOMSON COEFFICIENTS

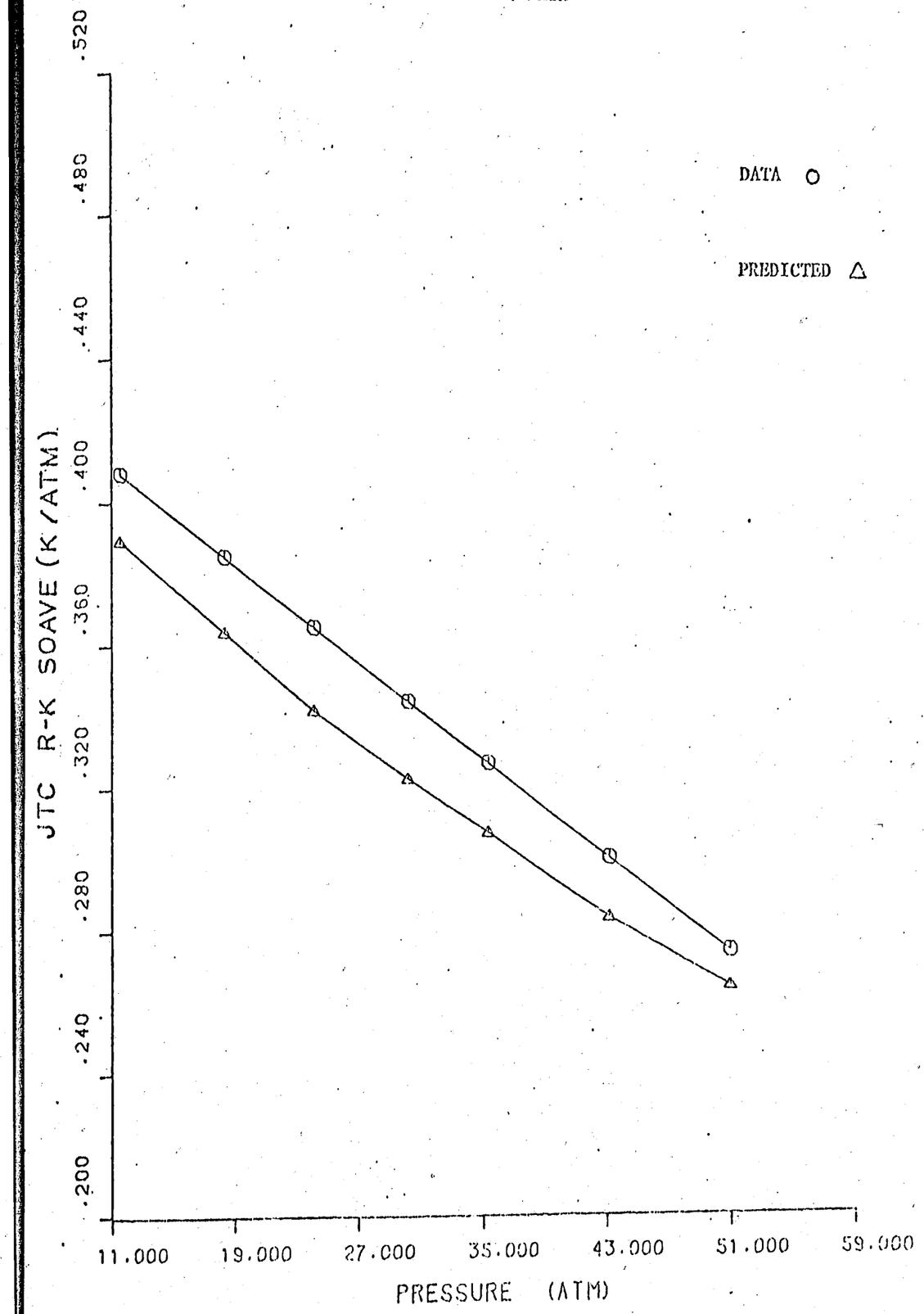
R-K PRAUSNITZ VS. DATA



RUN 4B

JOULE-THOMSON COEFFICIENTS

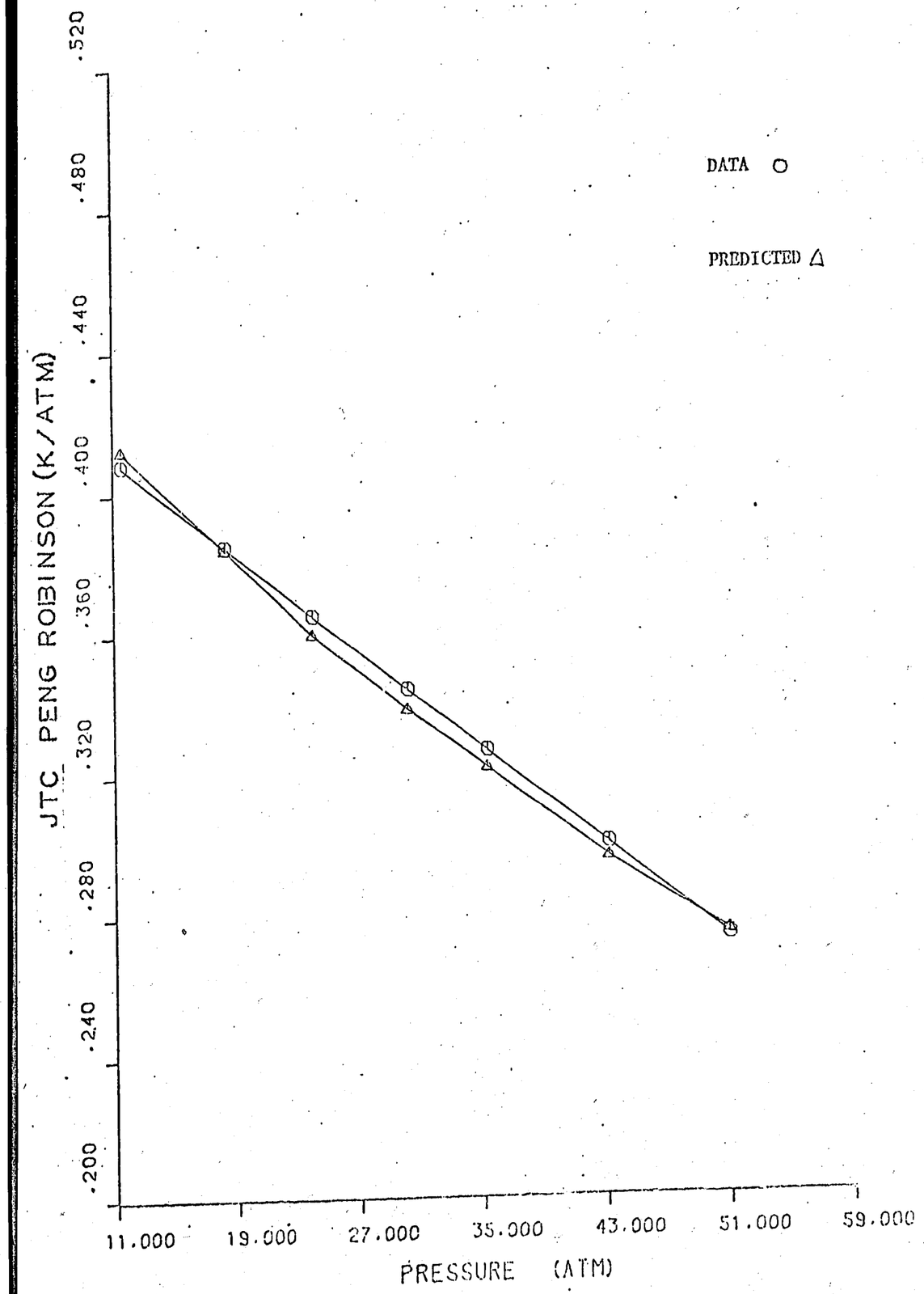
R-K SOAVE VS. DATA



RUN 4B

JOULE-THOMSON COEFFICIENTS

PENG-ROBINSON VS. DATA



RUN 4B

8. APPENDIX A

Table 8-1: TABLE of PARAMETERS

Data from Reed, et. al[16]

	Tc(K)	Pc(atm)	Ω_a	Ω_b	ω
CH4	190.65	45.4	0.4278	0.0867	0.013
H2	43.6	20.2	0.4278	0.0867	0.000

$K_{ij} = 0.03$

$\delta_{ij} = 0.14844$

R= 82.057 (atm-cc/gmole-K)

IDEAL HEAT CAPACITY

$Cp^o = A + BT + CT^2 + DT^3$ (cal / gmole-K) ; T(K)

	A	$Bx10^2$	$Cx10^6$	$Dx10^9$
CH4	4.598	1.245	2.860	-2.703
H2	6.483	0.2215	-3.298	1.826

Development of Expressions

Heat Capacity and Joule Thomson Coefficient

The general differential expressions for the heat capacity or Joule Thomson coefficient can be stated as:

$$\mu = \frac{(T(\frac{\partial V}{\partial T})_p - V)}{C_p}$$

We can express $(\frac{\partial V}{\partial T})_p = \frac{-(\frac{\partial P}{\partial T})_v}{(\frac{\partial P}{\partial V})_t}$

Therefore:

$$C_p = \frac{-T(\frac{\partial P}{\partial T})_v}{(\frac{\partial P}{\partial V})_t} - V$$

The heat capacity can be expressed as:

$$C_p = C_p^o - R - \frac{T(\frac{\partial P}{\partial T})_v^2}{(\frac{\partial P}{\partial V})_T} - T\int_v^\infty (\frac{\partial^2 P}{\partial T^2})_v \, dV$$

Clearly with the proper derivatives the expressions could be solved. These expressions were then applied to the Redlich-Kwong equation of state, both original and with the Soave modification; and to the Peng-Robinson equation of state.

Expressions for Heat Capacity and Joule Thomson Coefficient

Redlich-Kwong: Original

$$P=\frac{RT}{V-b}-\frac{a}{T^{0.5}V(V+b)}$$

$$C_p = C_p^o - R + \frac{0.75a}{T^{1.5}b}\ln\left(\frac{V+b}{V}\right) - \frac{T\left(\frac{R}{V-b}+\frac{0.5a}{T^{1.5}(V+b)V}\right)^2}{-\frac{RT}{(V-b)^2}+\frac{2a}{T^{0.5}(V+b)^2V}+\frac{ab}{T^{0.5}V^2(V+b)^2}}$$

$$C_p = \frac{\frac{-RT}{V-b}-\frac{0.5a}{T^{0.5}(V+b)V}+\frac{RTV}{(V-b)^2}-\frac{2a}{T^{0.5}(V+b)^2}-\frac{ab}{T^{0.5}(V+b)^2V}}{-\frac{RT}{(V-b)^2}+\frac{2a}{T^{0.5}(V+b)^2V}+\frac{ab}{T^{0.5}V^2(V+b)^2}}$$

With the Soave modifacation, a is not a constant, but a function of temperature.

$$a_m(T)=\sum_i\sum_j y_i y_j(1-K_{ij})(a_{ci}a_{cj}a_i(T)a_j(T))^{0.5}$$

$$a_{ci}=0.42747\,R^2\,T_{ci}^{\,2}\,P_{ci}^{\,-1}$$

$$a_i(T)=(1.+(m_i(1.-Tr_i^{\,0.5})))^2$$

$$m_i(\omega)=0.480+1.57\omega_i-0.176\omega_i^{\,2}$$

$$dP=(R/v-b)dT-(V(V+b))^{-1}\,da_m(t)$$

We can express the derivative of $a_m(t)$ as: Z * Q

$$Z = \sum\sum y_i y_j (1-K_{ij})(ac_i ac_j)^{0.5}$$

$$Q = \frac{-.5m_i - .5m_i m_j}{(Tc_i T)^{0.5}} - \frac{.5(m_j \pm m_i m_j)}{(Tc_j T)^{0.5}} + \frac{m_i m_j}{(Tc_i Tc_j)^{0.5}}$$

Hence:

$$\frac{dP}{dT} = R/(V-b) - (Z*Q)/(V(V+b))$$

$$\frac{dP}{dV} = \left(\frac{-RT}{(V-b)^2}\right) + \left(\frac{a_m}{(V(V+b))^2}\right)(2V+b)$$

$$\frac{d^2P}{dT^2} = Z\, dQ/(V(V+b))$$

$$dQ = \frac{.25m_i + .25m_i m_j}{(Tc_i{}^{0.5} T^{1.5})} + \frac{.25m_j + .25m_i m_j}{(Tc_j{}^{0.5} T^{1.5})}$$

Now by direct substitution we obtain:

$$C_p = C_p^o - R - \frac{T(\frac{dP}{dT})^2}{(\frac{dP}{dV})} - \frac{TZdQ}{b} \ln\left(\frac{V+b}{V}\right) \qquad \mu = \frac{(-T(\frac{dP}{dT}) - V(\frac{dP}{dV})}{C_p\,(\frac{dP}{dV})}$$

A similar procedure for the Peng-Robinson equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{(V+b)V + b(V-b)}$$

$$DPV = \frac{dP}{dV} = \frac{-RT}{(V-b)^2} + \frac{a(2V+2b)}{(V(V+b)+(V-b)b)^2}$$

$$DPT = \frac{dP}{dT} = \frac{R}{V-b)2} - (V(V+b) + b(V-b))^{-1} \frac{da}{dT}$$

$$a = \sum\sum y_i y_j a_{ij}$$

$$(i=j)\ a_{ij} = ac_{ii}\ a'_i$$

$$(i\neq j)\ a_{ij} = C(a_{ii}a_{jj})^{0.5}$$

$$C = (1. - \delta_{ij})$$

$$ac_{ii} = 0.45724\ (R\ Tc_i)^2 / Pc_i$$

$$a'_i = (1 + K_i(1 - Tr_i^{0.5}))^2$$

$$K_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

$$\frac{da_{ij}}{dT} = Da_{ij} =$$

$$(i=j) \qquad ac_{ii}\ da'_i = -K_i((ac_{ii}a'_{ii})^{0.5})(Tc_iT)^{-0.5}$$

$$(i\neq j) \qquad 0.5(ac_{ii}ac_{jj})^{-0.5}C(a'_j da'_i + a'_i da'_j)(a'_i a_{ij})^{-0.5}$$

$$Q = \sum\sum y_i y_j \, da_{ij}$$

$$DPT = \left(\frac{R}{V-b}\right) - \left(V(V+b) + b(V-b)\right)^{-1} Q$$

$$D2PT = \frac{d^2P}{dT^2} = -\left(V(V+b)+b(V-b)\right)^{-1} \frac{dQ}{dT}$$

$$DQ = \frac{dQ}{dT} = \sum\sum y_i y_j \left(\frac{d^2 a_{ij}}{dt^2}\right) = \sum\sum y_i y_j \, d2a_{ij}$$

$$d2a_{ij} = ac_{ij} \, d2a'_i$$

$$(i=j)\ d2a_{ij} = ac_{ij}\left(\frac{k_i a'^{0.5}_i}{Tc_i^{0.5}}\right)\left(\frac{0.5}{T^{1.5}} - \frac{K_i}{Tc_i^{0.5} T^{1.5}}\right)$$

$$(i\neq j)\ d2a_{ij} = (0.50)\left((a'_i a'_j)^{-0.5}(a'_j d2a_{ii} + 2da'_{ii} da'_{jj} + a'_i d2a'_j)\right.$$

$$\left. + \ (a'_j da'_i + a'_i da'_j) - 0.5(a'_i a'_j)^{-1.5}(a'_i da'_j + a'_j da'_i)\right)$$

Substituting into the equations we obtain:

$$C_p = C_p^{\circ} - R - T((DPT)^2/DPV) + T(DQ)(8b^2)^{-0.5} \ln\left(\frac{(2V+b+(8b^2)^{0.5})}{(2V+b-(8b^2)^{0.5})}\right.$$

$$\mu = (-(T(DPT)) - (V(DPV))/(C_p(DPV))$$

9. LIST of REFERENCES

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1. Alhert,R.C., Ph.D. Thesis, Lehigh University, Bethlehem, Pa. (1964)

2. Benham,A.L. and Katz,D.L., " A.I.Ch.E. Jour."3,33,(1957)

3. Brazinsky, I., M.A. Thesis, Lehigh University, Bethlehem, Pa. (1960)

4. Brief,A. and Joffe,J. " Jour. Chem. Eng. Data "15,1,(1970)

5. Chueh, P.H., and Prausnitz, J.M., " Ind. Eng. Chem. Fund." 6,492,(1976)

6. Eakin,B.E.,Devaney,W.E. and Bailey,N.L., " Proc. of 54th Gas Processors Conv. -Enthalpy Measurements of Synthetic Gas Mixture." Gas Pro. Assoc.,52,(1976)

7. Epstein, P.S.,Textbook of Thermodynamics, J.Wiley:London, 70,1937.

8. Gunn,R.D., Chueh,P.L. and Prausnitz, J.M.,"A.I.Ch.E. Jour.", 12,5,937,(1966)

9. Hoxton, L.G., "Physical Review" , Series 2,13,938,(1919)

10. Johnston, H.L. "Jour. Amer. Chem. Soc.",108,23102,(1949)

11. Kim, A.G. and Douglas, L.J. " U.S. Bureau of Mines: Report of Investigation",RI7903 , U.S. Dept. of Interior, (1974)

12. Muller,W.H.,Leland,T.W. and Kobayashi, R.," A.I.Ch.E. Jour.", 17,2,267,(1961)

13. Peng, D.Y, and Robinson, D.B., "Ind. Eng. Chem. Fund.",15 59, (1976)

14. Redlich,O.,Ackerman,F.S. et. al.,"Ind. Eng. Chem. Fund." 4,4,(1965)

15. Redlich, O. and Kwong, J.W.S.," Chem. Rev. ",44,233,(1949)

16. Reed,R.C.,Prausnitz,J.M. and Sherwood,T.K., The Properties of Gases and Liquids ,3rd.,McGraw-Hill:New York,629,1977.

17. Roebuck, J.R., "Proc. Amer. Acad. Arts and Science",60 527,(1925)

18. Soave, G.," Chem. Eng. Sci.",27, 6, 1197, (1972)

19. Stockett, A.L., Ph.D. Thesis, Lehigh University, Bethlehem, Pa. (1965)